

PATENT

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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**  
**BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES**

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Attorney Docket No.:

J3519(C)

Appellants:

Brownbill et al.

Serial No.:

09/737,649

Filed:

December 15, 2000

For:

HAIR BLEACHING AND COLORING COMPOSITIONS

Group: 1751

Examiner: Elisa B. Elhilo

Edgewater, New Jersey 07020

March 5, 2003

**BRIEF FOR APPELLANT**

Assistant Commissioner for Patents  
Washington, DC 20231

Sir:

There are enclosed herewith three (3) copies of an Appeal Brief for Appellants. Please charge \$320 fee to our Deposit Account No. 12-1155.

If additional fees are required, please charge the amount of such additional fees to Deposit Account No. 12-1155.

Three copies of this letter are enclosed.

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Respectfully submitted,

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PATENT

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March 3, 2003

**BRIEF FOR APPELLANTS**

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Group: 1751  
Examiner: Elisa B. Elhilo  
Edgewater, New Jersey 07020  
March 5, 2003

**BRIEF FOR APPELLANT**

Assistant Commissioner for Patents  
Washington, DC 20231

Sir:

This is a Brief on Appellant's Appeal from the Examiner's Final Rejection  
concerning the above-identified application.

### **I. REAL PARTY IN INTEREST**

The real party in interest is Unilever Home and Personal Care USA, Division of CONOPCO, Inc., a corporation of New York having a principal place of business at 325 North Wells, Chicago Illinois 60610, USA.

## **II. RELATED APPEALS AND INTERFERENCES**

There are no related appeals or interferences.

### **III. STATUS OF CLAIMS**

Claims 1-12, 15, and 16 are the subject of this appeal.

#### **IV. STATUS OF AMENDMENTS**

A Supplemental Amendment has been filed with the Appeal Brief requesting claims 13 and 14 be cancelled in order to bring the application into a better condition for appeal.



## **V. SUMMARY OF THE INVENTION**

The application is directed at the bleaching of hair or the combined bleaching and coloring of hair. Appellants have found a way to mitigate the damage to hair caused by high pH (>10) bleaching systems. High pH bleaching solutions were known to be desirable for effective and efficient decolorization of hair but had the drawback of causing excessive damage to the hair. Appellants have found that the incorporation of cholesterol and its derivatives produces a substantial reduction in hair damage of peroxygen bleaching systems that are buffered to a pH greater than 10.3. Thus, the core of the invention is the combination of appropriate peroxygen bleaching compounds, cholesterol and its derivatives, and a suitable buffering agent that maintains the pH greater than 10.3. Appellants claim bleaching compositions, combined bleaching and coloring compositions that utilize non-oxidative as well as oxidative dyes, kits that prepackage the ingredients, and methods of use of such compositions.

See page 2, lines 10-14, 23-27; page 3, lines 3-12; and pages 7-10, page 12-16.

## **VI. ISSUES FOR APPEAL**

Whether claims 1-12, 15, and 16 are obvious under 35 U.S.C. §103(a), over Lim et al. (U.S. Patent 5,961,666) and Anderson et al. (U. S. Patent 5,851,237).

## **VII. GROUPING OF CLAIMS**

Group I: Claims 1-6, 9, 10, 15, and 16

Group II Claims 7, 8, 11, and 12

### **VIII. APPELLANTS' ARGUMENTS**

**I. Whether Claims 1-6, 9, 10, 15, and 16 obvious under USC 35 §103(a) over Lim et al. (U.S. Patent 5,961,666) and Anderson et al. (U. S. Patent 5,851,237).**

Group I claims are directed exclusively towards bleaching compositions.

Both Lim et al. and Anderson et al. are directed at hair coloring compositions that employ specific oxidative dyes, couplers and a "developer" which is an oxidizing agent. Both Lim and Anderson are only concerned with coloring compositions, i.e., hair dye compositions which have the effect of coloring hair (see column 12, lines 21-25 in Lim and column 1 lines 6 to 14 in Anderson).

Lim et al. is concerned with hair dyes with good color and resistance. Thus, Lim et al. teaches a dyeing composition for keratinous fibers comprising 3-alkyl-4-aminophenol and 2 alkyl-1-naphthol (see column 2, lines 35-42).

The Examiner cites column 2, lines 35 to 38 of Lim et al. as teaching dye and bleaching compositions. However, the passage to which the Examiner refers does not disclose any bleaching compositions. The quoted passage in fact states that "...the color depth obtained from 3-methyl-4-aminophenol(3-Mepap) and 2 methyl-1-naphthol is as strong as 4-aminophenol on gray hair and significantly stronger on bleached hair". Notably, Lim et al. does not specify how the hair was bleached. Thus, Lim teaches coloring bleached hair, but not bleaching the hair.

Furthermore, the examiner has referred to the description of "dyed bleached tresses" at column 7, Table 1, line 45 in Lim et al. as reciting "hair bleaching compositions". The earlier description in this column states that the tresses in question are pre-bleached and the fact that they are bleached is not connected with the composition taught by Lim. Thus, Lim states that "the resulting mixture is *applied* to bleached and gray hair...." (see column 7, lines 22-23, emphasis added).

Anderson et al. is concerned with producing hair dyes comprising 1-(4-aminophenyl) pyrrolidines (see column 2 lines 46 to 51). According to Anderson such dye compositions provide advantages in terms of color and toxicity. Anderson only teaches the use of peroxygen compounds in connection with oxidative coupling, i.e., the development of the dye (see column 8, line 65 to 67). Thus, hydrogen peroxide is only suggested for use as a developer for the primary intermediate and coupler dye (see column 9, lines 2-5).

Thus, Lim and Anderson are concerned with compositions that contain as essential elements specific oxidative dyes that add color to the hair rather than compositions that remove color from the hair by bleaching.

Appellants' invention is directed at a long-standing problem, namely, "Hair bleaching and/or coloring compositions which deliver effective hair bleaching and/or coloring even on dark hair, but which avoid or reduce hair damage...." (Specification page 2, lines 13-17). Appellants have solved this problem by introducing cholesterol into a peroxygen bleaching solution buffered to a pH greater than 10.3 and preferable greater than 10.5 where such compositions can deliver effective bleaching, yet avoid or reduce hair damage

The Lim and Anderson references disclose hair dye compositions that contain hydrogen peroxide and cholesterol as optional ingredients, and can have a pH in range of 5-11. The Examiner has argued in the final rejection mailed September 26, 2002, that "...it would have been obvious to one having ordinary skill in the art at the time the invention was made to make such a composition because the reference teaches similar ingredients to those recited in the claims suitable for inclusion in a bleaching composition." The Examiner goes on to conclude "...thus, a person of ordinary skill in the art would expect such a composition to have similar properties to those claimed, absent unexpected results." Appellants respectfully maintain for the reasons set forth below that

without the benefit of hindsight, a person of ordinary skill in the art reading Lim or Anderson would not have been directed to appellants' invention.

Lim and Anderson are totally silent about how to make effective hair bleaching compositions, about the damage that can be caused by such compositions and about any ways whatsoever to mitigate this damage let alone specific compositions that achieve effective bleaching with reduced damage. Since both reference are concerned with adding color to the hair and not removing it, and neither reference mentions the problem or solution addressed by appellants' claim there would be no motivation for one of ordinary skill in the art to pursue the chemical mixtures presently claimed.

Lim and Anderson teach that the dye compositions may be weakly acidic, neutral, or alkaline but preferably the pH should be in the range of 8-10 (for example see Lim column 6, line 2). One of ordinary skill in the art would have been aware prior to the present invention that high pH can generally be damaging to hair. For example, J. Janchowicz, in his classic paper *Hair Damage and Attempts to its Repair* states on page 266 "The pH does not have a detectable influence on swelling in the range of 2-9. Further increase in pH, especially above 10, causes considerable damage.... Swellability of 40-50% above pH 10 probably signifies hydrolytic decomposition of the keratin structure and consequently loss of cohesion of fibrous material." More notably, Janchowicz goes on to state on page 270 "Although the purpose of bleaching is to eliminate color by the reaction of an oxidizing agent with the melanin pigment, side reactions significantly affect the properties of the keratin fibers. It is well established that hydrogen peroxide in conventional bleaching and oxidative hair dye formulations (alkaline media at pH 10 and above) leads to oxidative cleavage of disulfide bonds and the formation of cysteic acid as the end product. [J. Society of Cosmetic Chemists, **38** 263-286 (1987) – copy enclosed]. Since both Lim and Anderson prefer compositions having a pH between 8 and 10, one of ordinary skill in the art would have concluded that these references had not found a solution to the well documented problem of damage by pH > 10 bleaching solutions apart from keeping the pH below 10, and indeed none is mentioned.

There is no suggestion in Lim or Anderson that would have led one of ordinary skill in the art to pluck out cholesterol from among the lanolin derivatives, pantothenic acid and other general hair care ingredients referred to by reference, combine it with hydrogen peroxide and then raise the pH to at least 10.3, in order to arrive at appellants invention. Motivation to modify must come from the prior art. Specifically to select cholesterol in order to solve the problem of damage to hair at a pH >10 by bleaching agents.

Further, there is nothing in these references to lead one of ordinary skill in the art to expect the surprising result that cholesterol would be relatively more effective at preventing damage at a high pH (10.5) than at a lower pH (9.7). The surprising criticality of pH on the relative effectiveness of cholesterol in mitigating damage to hair is shown in Example 1 (page 15 Table 1 of specification). Notably, the reduction in hair damage by cholesterol is 10 times higher at pH 10.5 than it is at pH 9.7 but only about 3 time higher at pH 10.1. It is therefore entirely unexpected from a consideration of Lim and Anderson that the damage mitigating benefits of cholesterol would be obtained in bleaching systems operating at a pH >10, i.e., above the preferred pH range of Lim and Anderson.

The mere fact that one of ordinary skill in the art could in theory, formulate a hair bleaching composition by selecting from the range of nonessential and optional ingredients disclosed by Lim and Anderson is no reason to do so. The references provide no motivation to do so because there is no connection to the long-standing problem addressed by appellants' claims. There is no reasonable expectation of success following this approach because there is neither a suggestion in the references of how to proceed nor any glimmer of hope that such extensive experimentation would bear fruit. And finally, the results are unexpected based on the teaching of the references in issue not least of which is the fact that the largest relative effect of cholesterol in mitigating harshness occurs at a pH outside the preferred range taught by the references.

**II. Whether claims 7, 8, 11, and 12 are obvious under USC 35 §103(a) over Lim et al. (U.S. Patent 5,961,666) and Anderson et al. (U. S. Patent 5,851,237).**

Group II claims are directed at combining the less damaging bleaching or decolorizing compositions according to claims 1-6, with hair coloring agents to achieve hair coloring compositions, hair coloring kits, and methods of coloring hair.

In addition to the arguments presented above for the non-obviousness of appellants bleaching system over Lim and Anderson, the following further arguments are presented for the non-obvious of appellants claims directed to combined hair bleaching and coloring.

Lim and Anderson restrict the hair coloring agent to specific oxidative dyes, i.e., chemicals that are oxidized prior, during or after application to form a colored intermediate (see Lim column 3 lines 26-30 and specification page 7, line 30 to page 8, line 35). Appellants place no such limitation on the chemistry of the hair-coloring agent: both non-oxidative and oxidative dyes can be utilized (see specification page 7, line 18 through page 10, line 5).

Lim and Anderson are silent on the subjects of non-damaging bleaching compositions and non-oxidative dyes and thus there is no suggestion about combining these elements. Consequently, a person of ordinary skill in the art reading these references would not be directed to the combination of elements recited in appellants' claims at issue. Furthermore, replacing the dyes disclosed by Lim and Anderson by a non-oxidative dye would make these inventions inoperative, i.e., an oxidizing agent or "developer" would not oxidize a non-oxidative dye to form a colored intermediate.

As far as appellants' claims directed to bleaching and hair dying compositions employing oxidative dyes are concerned, these involve the selection of a narrow pH range (>10.3) from the broad pH range (acidic, neutral or alkaline) disclosed by Lim and



Anderson. In addition, a further selection, whereby cholesterol is chosen from the list of possible hair care substances is also necessary. There is no motivation in Lim or Anderson to make either of these specific selections let alone both. There is, in fact, a disincentive for this selection because both references teach that a preferred pH range is between 8 and 10.

## IX. CONCLUSION

Appellants respectfully request the Board of Patent Appeals and Interferences to reverse the Examiner's final rejection of claims 1-12, 15, and 16.

Respectfully submitted,

A handwritten signature in cursive script, reading "Michael Paul Aronson".

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**APPENDIX OF CLAIMS (37 C.F.R.. 1.192(c)(9))**

The text of the claim involved in the appeal is:

1. A hair bleaching composition comprising:
  - (a) a peroxygen compound;
  - (b) a buffering agent; and
  - (c) cholesterol and/or derivatives thereof or mixtures thereof;wherein the pH of the composition is greater than or equal to pH 10.3.
2. A hair bleaching composition according to claim 1, wherein the pH of the composition is greater than or equal to pH 10.5.
3. A hair bleaching composition according to claim 1 wherein the peroxygen compound is hydrogen peroxide.
4. A hair bleaching composition according to claim 1 wherein the buffering agent is ammonia.
5. A hair bleaching composition according to claim 1 further comprising at least one surfactant.
6. A method of bleaching hair comprising applying to the hair a composition according to claim 1.
7. A hair colouring composition comprising the hair bleaching composition according to claim 1 and additionally a hair colouring agent.
8. A method of colouring the hair comprising applying to the hair a composition according to claim 7.

9. A hair bleaching kit comprising:
- (a) a first package containing a peroxygen compound;
  - (b) a second package containing a buffering agent;
  - (c) cholesterol and/or derivatives thereof or mixtures thereof in the first and/or second package and/or in a third package;
- wherein the peroxygen compound, buffering agent and cholesterol and/or derivatives thereof or mixtures thereof form, when mixed, a hair bleaching composition according to claim 1 having a pH greater than or equal to 10.3.
10. A method of bleaching hair using a hair bleaching kit according to claim 9, comprising admixing the contents of the packages followed by applying the composition to the hair.
11. A hair colouring kit comprising:
- (a) a first package containing a water soluble peroxygen compound;
  - (b) a second package containing a buffering agent;
  - (c) cholesterol and/or derivatives thereof or mixtures thereof in the first and/or second package and/or in a third package;
  - (d) a hair colouring agent in the second package and/or third package and/or a fourth package;
- characterised in that the water soluble peroxygen compound, buffering agent, hair colouring agent and cholesterol and/or derivatives thereof or mixtures thereof form, when mixed, a hair colouring composition according to claim 7 having a pH greater than 10.3.
12. Method of colouring hair using a hair colouring kit according to claim 11, comprising admixing the contents of the packages followed by applying the composition to the hair.

15. A method of reducing damage to hair, protecting hair from damage or repairing damaged hair which comprises treating hair with bleaching and/or coloring compositions buffered to a pH of greater than 10.3 wherein cholesterol is added to the bleaching and/or coloring composition.
16. A composition, according to claim 15, wherein the pH is buffered to a pH of greater than about 10.5.

## Hair damage and attempts to its repair

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*Received February 10, 1987.*

### INTRODUCTION

The changes to the physical properties of hair fibers incurred as a result of weather, handling, and cosmetic treatments such as bleaching, waving, dyeing, or relaxing can be significant. In many instances they may lead to premature fracture of the hair, longitudinal fibrillation or separation of the hair cortex, loss of gloss, or increased absorption of moisture. The present paper is concerned with the identification of physical and physicochemical alterations in fiber structure and properties caused by a variety of degradative processes, reviewing the methods used to assess the extent of damage and identifying the treatments capable of stabilizing or enhancing the properties of hair fibers.

### CRITICAL ELEMENTS OF FIBER STRUCTURE AND THE PHYSICAL PROPERTIES OF UNDAMAGED HAIR

Hair fibers have two major morphological components, the cuticle and the cortex. The cuticle covers the whole fiber and is composed of layers of overlapping scales each about half a micron thick (1). In a newly formed fiber there may be as many as ten overlapping scales in a crosssection. The outermost layer of a cuticle cell is made up of a very thin membrane (3 nm) called the epicuticle. The next layer, exocuticle, consists of cystine-rich, highly crosslinked protein and represents about two-thirds of the cuticle structure (1,2). Beneath this, there is an endocuticle which has a low cysteine content and is mechanically the weakest part of the cuticle (2). Lastly, there is a thin layer of cell membrane complex. Both X-ray analysis and optical birefringence measurements have demonstrated the lack of molecular orientation in the cuticle (3,4). Some data exist which point to solvent-induced ordering during swelling (5).

The main function of the cuticle is to provide mechanical protection for the cortex. The role of the cuticle seems to be minor (2) in terms of contribution to the bulk longitudinal mechanical properties of the fiber as a whole. On the other hand, the cuticle has been shown to be an important factor in torsional mechanical properties of hair (6). While both the torsional modulus and logarithmic decrement exhibit no apparent de-

pendence on fiber diameter (in measurements conducted at 65% R.H.), an increase in the logarithmic decrement for fibers with a larger cuticle content was noted (6). Approximate calculation, based on the assumption that the torsional modulus of the whole, wet hair is  $1.8 \cdot 10^{10}$  pascals, yielded values for wet torsional moduli of  $2.4 \cdot 10^{10}$  pascals and  $1.2 \cdot 10^9$  pascals for the cortex and cuticle, respectively (6).

The cortex consists of elongated cortical cells, packed tightly together and oriented parallel to the fiber axis. They contain microfibrils, long uniform filaments which are hexagonally packed into units known as macrofibrils. The microfibrils are composed of highly crystalline material exhibiting a characteristic  $\alpha$ -helical X-ray pattern, and are embedded in an amorphous, cysteine-rich matrix. The moisture uptake of hair (14.5% at 65% RH) is confined mainly to the amorphous matrix and results in diametral swelling (16%), with fiber length affected to a minor extent (1.2%) (2).

The longitudinal mechanical properties of keratin fibers have been shown to be dependent upon temperature, humidity, and time-scale of the experiment and were studied by stress-strain methods (2). These have to be considered in terms of three distinct regions of strain (see Figure 1.). The stress-strain curve up to a few percent strain is referred to as the Hookean region. Further extension occurs with little increase in stress up to about 25–30% and is referred to as the yield region. This constant-stress region is thought to be associated with transformation in the microfibrillar regions.

Elongation beyond the yield region leads to a more rapid increase in stress as a function of strain and is called the post-yield region. Many workers attribute the post-yield

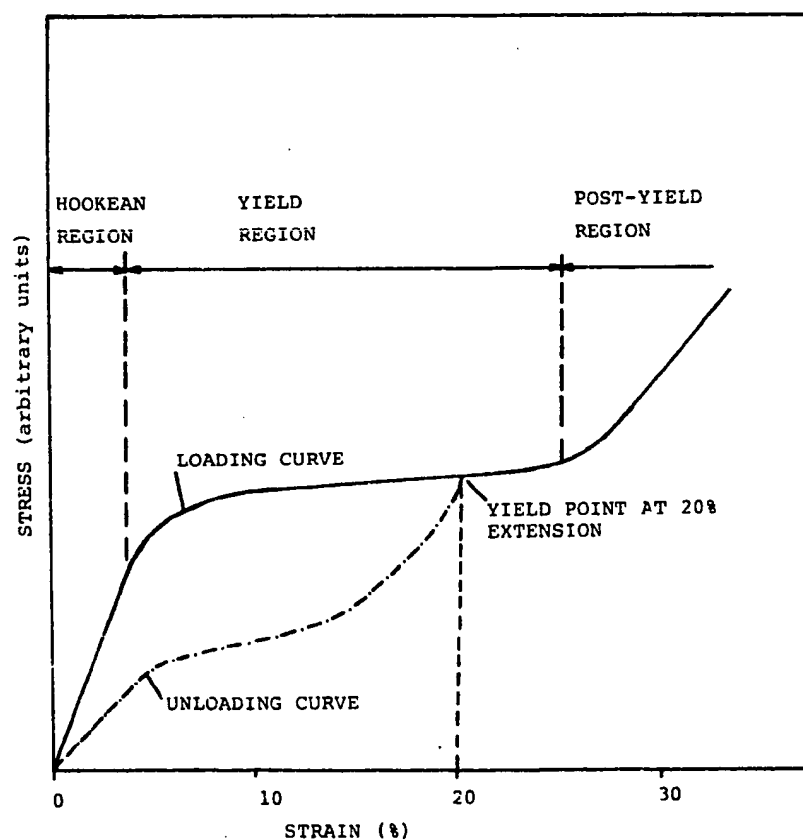


Figure 1. Stress-strain loading and unloading curves characteristic for human hair fibers.

region to the matrix. The ratios of the moduli of the linear portions of the three regions are approximately 100:1:10. Young's modulus for wool fibers in water was found to vary in the limits  $1.7-2.0 \cdot 10^9$  pascals, depending upon the rate of strain. As the content of water in the keratin structure is reduced, the stiffness of the fiber increases. In completely dry fibers (0% RH), Young's modulus is augmented by a factor of about 2.7 relative to the same modulus in water. The reference crosssectional area in both cases is the value for the wet fibers. It should be noted, however, that the equilibrium stiffness of the fibers (obtained under static conditions and independent of the rate of strain) is independent of the moisture content and corresponds to a value of  $1.4 \cdot 10^9$  pascals (7).

It was reported by Feughelman *et al.* (2) that  $6-7 \cdot 10^8$  pascals of equilibrium Young's modulus value of  $1.4 \cdot 10^9$  pascals are due to coulombic interactions between positively and negatively charged groups in the side-chains of the polypeptides in the keratin structure. Thus, hair fibers tested in aqueous media in the pH range 1-3, the conditions under which carboxylic residues are undissociated, showed a 40% decrease in Young's modulus.

The mechanical behavior of keratin fibers is often considered in terms of a two-phase model consisting of a water-impenetrable phase of cylindrical rods (microfibrils) oriented parallel to the fiber axis, embedded in a water-penetrable matrix phase (8). According to the predictions of this model, in longitudinal extension the two phases act in parallel and are equally deformed. In other words, in the wet state, the crystalline phase (microfibrils) contributes considerably to the longitudinal stiffness of the fiber. When the fiber is subjected to torsional stress, on the other hand, and if the matrix is weakened by the presence of water, distortion is confined to the matrix. In agreement with the experimental data, the presence of water in the keratin fiber structure should cause a greater reduction in torsional rigidity than in longitudinal stiffness. Based on dynamic mechanical analysis carried out at various humidities, and on conventional mechanical tests at different temperatures in water, estimates have been made of the mechanical contribution of each phase to the equilibrium Young's modulus of  $1.4 \cdot 10^9$  pascals (2). According to these calculations, the contribution of the microfibrils is close to  $1.2 \cdot 10^9$  pascals (about 85% of the equilibrium Young's modulus) and the matrix contribution is of the order of  $0.2 \cdot 10^9$  pascals (only about 15%).

## PHYSICAL AND PHYSICOCHEMICAL METHODS FOR DETECTION OF FIBER DAMAGE

### STRESS-STRAIN RELATIONS

The measurement of the longitudinal mechanical properties of hair is frequently applied to assess the damaging effects of chemical treatments. Several parameters calculated from stress-strain data were reported to be sensitive to modifications of fibers as a result of cosmetic treatments or environmental degradation. The most commonly used were 20% index, which is the ratio of work required to stretch the fiber by 20% after treatment to the work required to stretch the fiber by 20% before treatment (9), the yield point (stress) at 15% elongation (10), and the tensile strength or extension to break (10).

Deem *et al.* (11) introduced a new parameter, hysteresis ratio ( $H_{20}$ ), for the mechanical



testing of untreated and modified hair in the wet state. It is defined as the ratio of work regained in unloading from 20% extension to the work required to extend by 20% ( $W_{20}$ ; see loading and unloading stress-strain curves in Figure 1). The authors studied the effect of various degradative and nondegradative treatments such as bleaching, reduction and blocking, reactions with ninhydrin, formaldehyde, phenylisocyanate, mercuric acetate, etc. on the hysteresis ratio and its dependence on temperature. For untreated hair, the loading and unloading curves yield an increasing hysteresis ratio with increasing temperature. This study showed that the work of unloading and especially the shape of the unloading curve vary appreciably with temperature and chemical modification. It was also suggested from a spring-dashpot model of a keratin fiber that the apparent second-order phase transition, observed by plotting the hysteresis ratio versus temperature, is related to a change in the viscosity of the matrix.

#### DYNAMIC MECHANICAL MEASUREMENTS

A rocking beam oscillator, an apparatus originally developed by Tokita (12), was applied to the study of untreated and modified hair fibers (13). The measurements performed at low strain and 75% RH yield values of longitudinal elastic modulus ( $E'$ ) and of loss modulus ( $E''$ ), a measure of the irreversible loss in energy when the fiber is extended. For virgin hair at 25°C,  $E'$  and  $E''$  were found to be  $(4.1 \pm 0.66) \cdot 10^{11}$  pascals and  $(0.177 \pm 0.027) \cdot 10^{11}$  pascals, respectively. Considerable scatter in the values of  $E'$  and  $E''$  was ascribed to difficulty in accurately determining the cross-sectional area of the keratin fiber. The technique was sensitive to hair modifications involving binding of organic molecules, reduction, and impregnation of hair with polymer.

The values of the real ( $G$ ) and imaginary ( $G'$ ) parts of the torsional modulus determined under dry and wet conditions provide useful information about the matrix, the water-accessible phase of the fiber (6,14). The measurements were performed by the use of a free-swinging torsional pendulum. For virgin hair at 25°C and 65% RH, the torsional modulus  $G$  and logarithmic decrement  $\delta$  (related to the loss modulus  $G'$  by the equation  $G' = G\delta/\pi$ ) were found to be  $(1.02 \pm 0.09) \cdot 10^{11}$  pascals and  $0.4 \pm 0.05$  respectively. The data reported for heat-set, bleached, dyed, waved, and relaxed hair demonstrated that the changes in both  $G$  and  $G'$  can be related to the configurational stability in water and can be of some utility in predicting the setting behavior of hair.

#### SWELLING MEASUREMENTS

The swelling of hair in water, determined by the liquid retention technique, was found to be in the range 31–33 percent (15). The experimental procedure involves measuring the amount of liquid retained by hair after a 30-min equilibration in water or other specified solvent. The pH does not have a detectable influence on swelling in the range 2–9. Further increase in pH, especially above 10, causes considerable expansion. Reduction of pH below 2 results in a slight increase in swelling. Swellability of 40–50% above pH 10 probably signifies hydrolytic decomposition of the keratin structure and consequently loss of cohesion of fibrous material. This method had been applied to

determine the extent of loss in crosslinking density in wool keratin from reduction, bleaching, dyeing etc.

#### FRICITION AND COMBABILITY MEASUREMENTS

Inter-hair friction measurements, performed by the twist method of Lindberg and Gralen (16), provided useful information about the degree of cuticle damage and the response of hair fibers to physical handling (17). Static and kinetic coefficients of friction for root-to-tip and tip-to-root directions were calculated and used to interpret chlorine-hair interactions.

Combing work or force determination can also be a good indication of the degree of surface modification or damage. The details of experimental techniques, which consist of suspending a hair swatch from a force-measuring device, inserting a comb close to the root end of the swatch, setting the comb in a straight-combing motion through the swatch at a constant speed, and continuously recording the forces that resist its motion during transit from the point of insertion till it clears the tip end of the swatch, were described in a few papers (18,19). The experiments can be performed on dry hair at constant relative humidity or on wet samples, and should be referenced to a control swatch of untreated hair. This method is sensitive to the presence of surface deposits which can either decrease (lubricants such as cationic surfactants or silicon oils) or increase (dye or polymer deposits) the frictional coefficients and, consequently, combing forces (20).

#### THERMOMECHANICAL ANALYSIS (TMA), DIFFERENTIAL THERMAL ANALYSIS (DTA), AND THERMOGRAVIMETRIC ANALYSIS (TGA)

TMA, DTA, and TGA were utilized to assess thermally-induced viscoelastic and dimensional transitions in untreated and modified keratin fibers in the temperature range  $-50$  to  $325^{\circ}\text{C}$  (21). In the TMA experiment, penetration and extension thermograms showed two transitions, at  $59-72^{\circ}\text{C}$ , corresponding to side-chain motions of the proteins, and at  $242^{\circ}\text{C}$ , resulting from melting of the  $\alpha$ -helix. The low-temperature TMA transitions were covered under the broad DTA endotherm and are not distinguishable in the TGA analysis except for about 10% weight loss, presumably related to water evaporation. The high-temperature TMA transitions are also evident as an inflection in the TGA and two sharp endotherms in DTA traces.

#### ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS (ESCA)

This technique provides valuable information about the hair surface to a depth of 20 to 30 Å (22). It involves irradiation of a fiber with X-rays of known energy, which causes core electrons to be ejected from the sample. Their binding energy is related to specific atoms and functional groups, thus unraveling the chemical composition of the fiber surface. In the case of human hair, this technique was found useful to study the oxidation of disulfide sulfur during bleaching, removal of lipid from hair, and weathering by UV radiation (22).

## SCANNING ELECTRON MICROSCOPY (SEM) AND TRANSMISSION ELECTRON MICROSCOPY (TEM)

Scanning electron microscopy, because of its high resolution, wide range of magnifications, and high depth of focus, has been widely used to examine the architecture of the hair surface (cuticle), geometrical dimensions of fiber crosssections (determination of major and minor axis length), and characterization of fiber fractures (23–28). It is a valuable tool to study the alterations in fiber morphology due to cosmetic treatments. Gould *et al.* (28) used TEM in conjunction with image analysis to quantitate the effect of weathering or shampooing on the number and geometrical dimensions of voids in the cuticle and in the cortex. Brown and Swift (26) obtained SEM stereo-pair micrographs to facilitate the interpretation of the three-dimensional surface morphology of the fibers.

## FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Infrared spectroscopy has been applied to evaluate keratin oxidation by a number of investigators (29–32). Recently, a high-pressure diamond anvil cell and FTIR instrument were used to quantify the extent of transformation of various specific functional groups in the hairs' structure (32). The following bands were referenced against peptide bands ( $1650\text{ cm}^{-1}$ , corresponding to amide I band;  $1230\text{ cm}^{-1}$  corresponding to amide III band; and  $1076\text{ cm}^{-1}$ ) and were used to determine the Bunte salt content and the effect of bleaching and weathering on hair: the symmetric and asymmetric sulphonate  $\text{S} = \text{O}$  stretching vibrations at  $1040\text{ cm}^{-1}$  and  $1188\text{ cm}^{-1}$ , the bands at  $1219\text{ cm}^{-1}$  and  $740\text{ cm}^{-1}$  assigned to cysteic acid moiety, the bands at  $1196\text{ cm}^{-1}$ ,  $1022\text{ cm}^{-1}$ ,  $633\text{ cm}^{-1}$ , and  $522\text{ cm}^{-1}$  assigned to the asymmetric  $\text{S} = \text{O}$  stretch,  $\text{S} = \text{O}$  symmetric stretch,  $\text{S} = \text{O}$  symmetric deformation, and the  $\text{S} = \text{O}$  asymmetric deformation vibrations of thiosulphate ions (Bunte salt).

## SORPTION MEASUREMENTS

Copper and polymer uptake by hair was reported to be related to the extent of damage caused by oxidizing and reducing agents (9,33,34). For copper ions,  $\text{Cu}^{+2}$ , the equilibrium uptake was found to be dependent on the concentration of the treatment solution, temperature, or pH, and varied in the range 40–60 mg Cu/g hair (9). Equilibrium cationic polymer uptake of untreated hair was found to be in the range 2–3 mg/g, depending on the pH of the treatment solution. The cationic polymer uptake increased significantly to up to 10 mg/g for bleached fibers (34).

## ALKALI SOLUBILITY

The alkali solubility test was proposed by Overbeke *et al.* (35) to evaluate oxidative damage in wool fibers. It consists of treating the fibers with 0.1 N NaOH at  $60^\circ\text{C}$  for 1 hour and measuring the weight loss. This test has also been used to assess the extent of structure alteration in bleached hair (9).

## CHANGES IN STRUCTURE AND PROPERTIES OF HAIR AFTER DAMAGE

## PHYSICAL HANDLING (CLEANSING, BRUSHING, AND COMBING)

Weathering, brushing, combing, and cleansing results primarily in changes to the surface architecture of human hair. Swift and Brown (36), Robinson (37), and Garcia *et al.* (27) determined that there is a gradual change in surface structure as a function of the distance from the scalp (from root to tip). Their analysis is based on SEM micrographs of long-hair samples subjected only to normal hair care treatments of brushing, combing, and use of a shampoo containing a conventional anionic detergent. The portions of the fiber close to the scalp are sleek, the scales imbricate with free edges of relatively smooth contour. At increasing distance from the scalp, the scales become more damaged, with jagged edges, sometimes lifted away from the underlying layers. Scratch marks parallel to the fiber axis can often be observed. At the tip ends, the scales are frequently eroded away, the fibers sometimes split into many fibrous elements. Typical morphological features of damaged hair fibers are illustrated by micrographs presented in Figure 2. These destructive alterations to the hair surface are believed to arise from brushing, combing, and handling in the wet state (36). Some contribution to this deterioration may be due to weathering by exposure to rain, sunlight, and dirt, although results indicate that wet abrasion accompanying shampooing and towel drying alone, with minimal combing and no exposure to sun or rain, can cause similar damage.

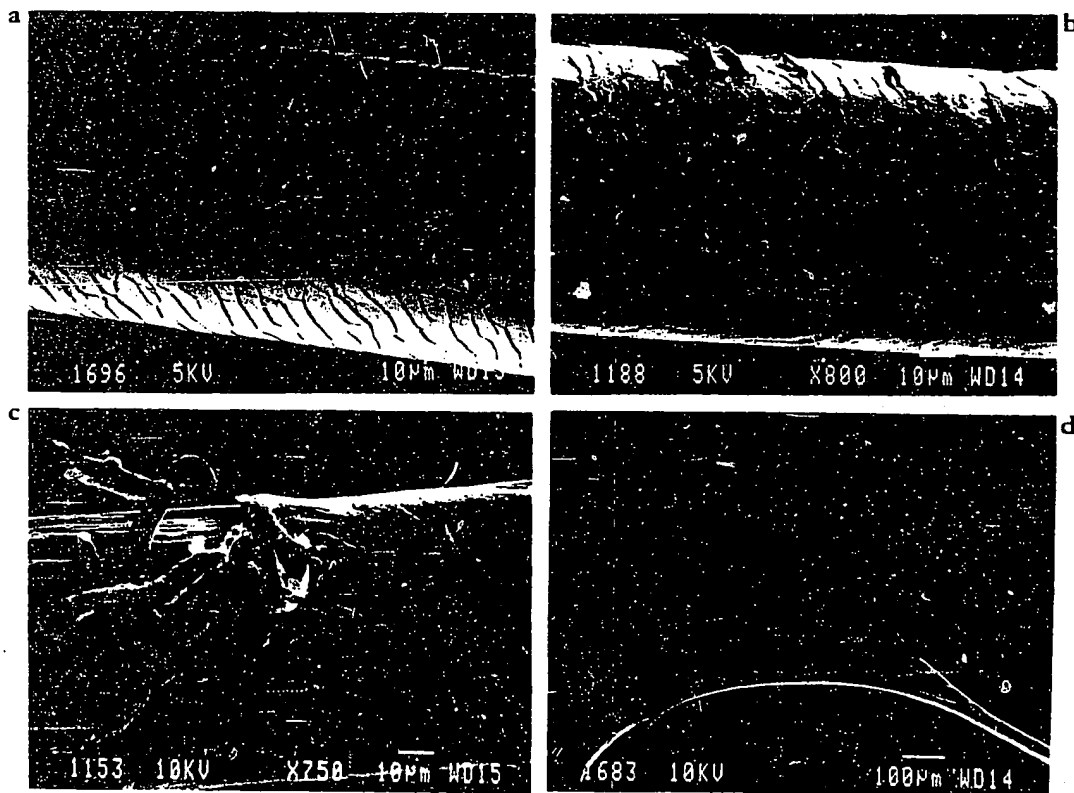


Figure 2. SEM micrographs of hair fibers illustrating various types of damage: a) intact hair fiber; b) fragment of hair fiber with partially removed cuticle, lifted scales, and scratch mark exposing cortex; c) fragment of hair fiber with eroded scales and early stages of longitudinal splitting into fibrous elements; d) split end.

Rubbing of dry fibers results in cuticle loss near the fiber tips, although it does not produce the same degree of scale damage. SEM examination of tangled hair has demonstrated that when hairs become twisted around each other, grooves can form in the cuticle surface, and in some cases cuticle can be removed. In dynamic combing experiments, abrasion and deformation of the fibers has been shown to cause stripping of cuticle and fracturing of the fibers. It appears that the types of fracture that result from this treatment yield longitudinal splitting. The average rate at which the scale margins recede down the fiber by combing is about  $0.5 \mu\text{m}/2000$  comb strokes.

Structural deformation of hair fibers under various conditions of mechanical stress were studied by SEM (26). Hair samples were clamped between the crosshead and load cell of an Instron tensile tester and extended at various rates until fracture occurred. Five main types of fracture, related to the degree of internal damage as a result of weathering, were observed. These were: (1) clean transverse fracture in the case of less weathered hair samples; (2) clean transverse fracture with some disturbance of cuticle; (3) part of the fracture is transverse but the remainder tails off with segments of cortex pulled off (also, the damage to cuticle is more severe in the form of lifting as well as longitudinal and circumferential splitting); and (4,5) fracture ragged with cortex separating into fibrillar elements (such a fracture pattern was observed in the case of severely weathered hair (26)).

Negroid hair is especially prone to damage during grooming procedures because of a high frequency of kinks along the fiber axis and its ribbonlike cross-sectional shape (38). Such a unique fiber configuration leads to extensive entanglements which increase the forces applied during combing. The fracture behavior of negroid hair was studied by tensile-fatigue measurements and SEM (38). These studies revealed that frequent twists with random reversals in direction and pronounced flattening in the region of twist lead to stress concentrations during tensile deformation. Fiber failure at low extensions is due to the initiation of cracks at numerous weak points near the twists. SEM showed the predominance of step fractures and a large proportion of fibrillated ends which reflect poor cohesion between cortical cells. In contrast, undamaged caucasian hair usually produced smooth transverse fractures.

#### BLEACHING

Although the purpose of bleaching is to eliminate or lighten the natural hair color by the reaction of an oxidizing agent with the melanin pigment, side reactions significantly affect the properties of the keratin fibers. It is well established that hydrogen peroxide in conventional bleaching and oxidative hair dye formulations (alkaline media at pH 10 and above) leads to oxidative cleavage of disulfide bonds and the formation of cysteic acid as the end product (29). According to aminoacid analysis, extensive bleaching can reduce the content of half-cystine residues from 13.9% to 5%, which corresponds to approximately a 64% reduction in the disulphide bond linkages of the protein molecules (10,39). Bleaching also reduces the concentration of free sulfhydryl groups (for example, from  $2.46 \mu\text{mol}/\text{mg}$  to  $0.3 \mu\text{mol}/\text{mg}$  (39)). Qualitatively similar results were reported by Robbins *et al.* (40) and Wolfram (41). The oxidative scission of disulfide bonds results in decreasing the crosslink density of the protein and provides additional anionic sites in the form of cysteic acid residues. Both reduction in covalent crosslink density and an increase in hydrophilicity contribute to the increase in swelling

(liquid retention) (10), alkali solubility (9), and sorption of metal ions (9) as well as polymers (34). For bleached hair, liquid retention was found to be about 42–43% in the pH range 3–5, with increases of up to 52% in the pH region of 5–7.5 (10). For untreated hair, an increase in swelling above 31% is observed at pH values above 9. The phenomenon of increased swelling and its pH dependence for bleached hair has been explained by the charge-rearrangement mechanism postulated for oxidized wool by Thomson and O'Donnel (42). According to this mechanism, strongly acidic cysteic acid residues displace carboxylic groups from their salt links with ionized basic groups. The carboxyl groups remain essentially unionized at pH 4 and below, due to the increase in negative charge density following the formation of cysteic acid residues. Above pH 5, the displaced carboxylic groups begin to titrate, bringing about an increase in swelling. In addition, it has also been proposed that the oxidative destruction of the melanin granules might result in the formation of discrete voids within the fiber structure which contribute to the swelling characteristics (10).

Moisture absorption (regain) parallels the trends recorded in swelling measurements and increases with the extent of bleaching over a wide range of humidities, 17–94%. At 61% RH regain increases from 13.5% for intact hair to 14.8% for bleached fibers (10).

The wet strength of keratin fibers is determined to a great extent by the concentration of disulfide bonds which form crosslinks. On the other hand, the strength of dry fibers is not appreciably influenced by the density of covalent crosslinks and depends largely on Van der Waals forces and ionic interactions between the peptide chains. Consequently, for bleached hair, in which the disulfide bonds have undergone oxidative scission by hydrogen peroxide or peracetic acid, a steady decrease in wet strength (yield stress, stress at breakpoint, and 20% index) with increased time of bleaching is observed (10). For example, the yield and stress at break decrease from 1.1 g/den to .99 g/den and from 1.9 g/den to 1.4 g/den, respectively, for hair bleached with  $\text{H}_2\text{O}_2$  at pH 10 for 60 min. The reduction in fiber strength is accompanied by an increase in the extension to break by a few percent, from 51.5–53.5% to 57.5–59.5%. The modulus, ultimate strength, and breaking extension of dry fibers are virtually unaffected by the same treatments.

Since the hydration of bleached hair is strongly pH-dependent, it is also reflected in the mechanical performance of wet fibers. Bleached hair exhibits a region of maximum mechanical stability between pH 3 and 5, where the displaced carboxylic groups are undissociated and those ionized are bound in salt links. Above pH 5 the ionization of free carboxyl groups occurs, leading to increased fiber hydration and reduction in fiber strength (10).

Another parameter deduced from stress-strain relations, the hysteresis ratio at constant temperature, was found to be independent of the number of bleaching treatments, but the absolute value of  $W_{20}$  decreases by as much as 35% with increasing bleaching (11). Bleaching raises the temperature of the second-order phase transition from 46°C to 56°C. An increase in the transition temperature was also reported for  $\text{H}_2\text{O}_2$ -oxidized hair in TMA measurements (21).

Similar trends are evident from dynamic mechanical measurements (6). The torsional modulus of bleached hair, at 65% RH, was  $(1.05 \pm 0.005) \cdot 10^{11}$  pascals and does not differ from that determined for intact hair  $((1.02 \pm 0.09) \cdot 10^{11}$  pascals). For wet hair, the decrease in rigidity ratio (the ratio of wet to dry torsional moduli) from  $0.26 \pm$

0.01 for intact hair to  $0.14 \pm 0.01$  for bleached hair is pronounced. The logarithmic decrement, on the other hand, was virtually unaffected by bleaching and changed from  $0.40 \pm 0.05$  for intact hair to  $0.44 \pm 0.03$  for bleached fibers.

#### WAVING

In cosmetic practice, the waving of hair is usually accomplished by the fission of disulfide bonds by reaction with mercaptans. The reagent most frequently used for this purpose is thioglycolic acid (0.6–0.8 M at pH 9.1–9.5). The rate of reaction is diffusion-controlled under alkaline conditions, and full penetration into hair usually requires 15–20 min (41). According to amino acid analysis, the concentration of half-cystine residues in TGA-reduced hair may decrease by as much as 40% (from  $156.4 \pm 4.5$  mol/1000 mol total amino acids analyzed to  $95.8 \pm 0.1$  mol/1000 mol total amino acids analyzed) (39,43). This is accompanied by an increase in concentration of free thiol groups from  $2.46 \mu\text{mol/mg}$  to  $506.5 \mu\text{mol/mg}$  (39). Thiol groups can be easily oxidized by atmospheric oxygen, and thus the stabilization of reduced hair properties usually involves the blocking of thiol groups by reaction with iodoacetic acid or crosslinking with dihalogenoalkanes (diiodomethane, dibromoethane, or dibromohexane) (11,21). In a permanent-waving procedure, disulfide crosslinks are rebuilt by the use of a suitable oxidizing agent such as sodium bromate, hydrogen peroxide, etc. The neutralization (oxidation) step reinstates most of the original disulfide bridges, with concomitant reduction of the number of thiol groups.

The mechanical properties of reduced, reduced-blocked, reduced-crosslinked, and permanent-waved (reduced and reoxidized) hair were studied by measurement of stress-strain relations and calculation of hysteresis ratios (11). In general, for reduced and blocked or crosslinked hair, a considerable decrease in  $W_{20}$  and a small increase in  $H_{20}$ , as compared to untreated hair, is observed ( $W_{20}$  and  $H_{20}$  changed from 350 to 149–316 and from 0.524 to 0.558–0.624, respectively, at 25°C, depending on the choice of mercaptan. Considerable differences in  $H_{70}$  between treated and untreated hair occur at temperatures below the transition temperature.  $W_{20}$  and  $H_{20}$  of hair reduced with either thioglycolic acid, phenyl mercaptan, or ethyl mercaptan, and subsequently blocked with iodoacetic acid, were similar. Benzyl mercaptan caused a larger reduction in  $W_{20}$  and also effected an appreciable change in  $H_{20}$  at various temperatures. Reduction and blocking also decreased the transition temperature from 46°C to 38–43°C, depending on the mercaptan. Reduction and crosslinking provided mixed results, producing an increase in transition point to 48°C for treatments involving diiodomethane and dibromohexane and a decrease to 41°C for crosslinking with dibromoethane.

A study of dry reduced hair using the oscillating beam method showed a small decrease in  $E'$  from  $(4.1 \pm 0.66) \cdot 10^{11}$  pascals to  $(3.5 \pm 0.2) \cdot 10^{11}$  pascals and no change in  $E''$  (13). In the case of hair treated with a waving lotion, which involves reduction followed by reoxidation, no difference in either  $E'$  or  $E''$  was detected, suggesting that the system has returned to its original mechanical state even though its internal and external configuration may have changed. Similar conclusions can be drawn from torsional modulus determinations in air at 65% RH, which also demonstrated no significant change from  $(1.02 \pm 0.09) \cdot 10^{11}$  pascals for waved hair (6). On the other hand, rigidity ratios in water and 0.1N HCl were found to be dramatically reduced from 0.26

$\pm 0.01$  (waved hair) and  $0.16 \pm 0.01$  (untreated hair) to  $0.09 \pm 0.01$  and  $0.06 \pm 0.01$ , respectively. Destabilization of the fiber structure in HCl solution can be interpreted as due to breaking of salt linkages. The reduction of rigidity ratios is accompanied by an increase in the logarithmic decrement in water from 0.40 to 0.56.

Reduction with 0.1M TGA followed by alkylation with iodoacetic acid reduced the softening temperature from 242°C to 225°C and increased the expansion at 256°C from 54% to 86% in TMA experiments. However, no shift in low-temperature transition was detected. Lowering of the high-temperature transition corresponds to melting of the  $\alpha$ -helices and has been interpreted as being consistent with the idea that disulfide crosslinks are converted to thiol groups by reducing agents, resulting in a structure that is less stable. Samples not reacted with iodoacetic acid, to block reoxidation, did not differ from the control, untreated hair. Similar dependencies were noted in DTA experiments with reduced wool fibers (44).

#### DYEING

There is a genuine scarcity of published information on the effect of dyeing on the physical properties of hair. Among three types of dyeing compositions, permanent (oxidative), semipermanent, and surface, only the oxidative systems are able to produce irreversible, deleterious changes in the fiber structure. Such alterations are expected to be similar to those produced by bleaching, although on a smaller scale. This hypothesis seems to be substantiated by torsional measurements of hair (6). Measurement of the torsional modulus at 65% RH shows no significant difference between control ( $1.02 \pm 0.09 \cdot 10^{11}$  pascals) and blond ( $1.07 \pm 0.05 \cdot 10^{11}$  pascals) or black-dyed ( $1.08 \pm 0.13 \cdot 10^{11}$  pascals) hair. Rigidity ratios are slightly reduced to  $0.23 \pm 0.01$ , as compared to those obtained for untreated hair ( $0.26 \pm 0.01$ ), and probably reflect a decrease in crosslink density caused by the action of hydrogen peroxide. Bleaching produces more extensive degradation of the fiber integrity by reducing the rigidity ratio to  $0.14 \pm 0.01$ . Although no numerical data are available, oxidative dyeing should also result in an increased swelling capacity.

Probably the most important aspect of the damaging effect of dye compositions on the properties of hair is their ability to form dye deposits on the fiber surface which can considerably increase the frictional coefficient and, consequently, combing forces (20). The measurements of dry and wet combing work revealed a few hundred percent increase in combing forces for hair treated with oxidative dye compositions (20). This problem, however, can be circumvented by the post-dyeing application of suitable conditioners.

#### ALKALINE RELAXING OR STRAIGHTENING

Hair straightening formulations for African-type hair which employ strong alkali such as sodium hydroxide (or combination of carbonates and guanidine) as active ingredient are referred to as hair relaxers. The interaction of such compositions with hair involves primarily alkaline fission of disulfide bonds which can occur either by hydrolysis or nucleophilic substitution of sulphur by hydroxide ion,  $\alpha$ -elimination consisting of the initial abstraction of the  $\alpha$  proton followed by heterolytic cleavage of the  $-S-S-$



bond, or  $\beta$ -elimination involving abstraction of the  $\beta$  proton followed by elimination of the unstable disulfide anion and formation of dehydroalanine (41). Other hair-structure damaging reactions might be related to peptide-bond hydrolysis. Alkaline scission of the disulfide bond brings about a reduction in half-cystine content (as high as 72% (39)), with a concurrent increase in the free thiol content to 70.3  $\mu\text{mol/mg}$ .

Destabilization of the relaxed hair structure is evident from torsional mechanical analysis (6). The torsional modulus measured in hair at 65% RH was reduced from  $(1.02 \pm 0.09) \cdot 10^{11}$  pascals to  $(0.91 \pm 0.11) \cdot 10^{11}$  pascals by alkaline relaxing. A decrease in wet fiber strength is more pronounced and is reflected in a decrease in the rigidity ratio in water from  $0.26 \pm 0.01$  to  $0.06 \pm 0.02$ , with a concomitant increase in the logarithmic decrement from  $0.40 \pm 0.05$  to  $0.65 \pm 0.04$ .

SEM analysis of relaxed hair, with cuticle cells removed by formic acid treatment and sonication, revealed extensive damage to the cortex manifested as fraying of large-fiber bundles (39). Reduced crosslink density of the cuticle and cortex also leads to increased swelling, which makes the fibers more susceptible to surface damage during normal handling procedures.

#### PHOTODEGRADATION

Prolonged exposure of keratin to sunlight or UV irradiation leads to destructive changes in the keratin structure (45–47). Mechanistic studies suggest interaction of light with disulfide bonds (47–51), deamination or decarboxylation of aminoacids (52), disorientation of hydrogen bonds, and chemical alterations of the aromatic nuclei in tyrosine and phenylalanine (53). The recent application of ESCA to investigate the process of UV oxidation of hair revealed an extensive conversion of S(II) to S(IV), which is consistent with the hypothesis that UV light is primarily responsible for the oxidation of sulfur in weathering of human hair (22). Beyak *et al.* (47) used the stress value at 15% elongation (yield point at 15% strain), determined on the basis of stress-strain curves, to assess the extent of damage after a few months exposure to solar radiation. They demonstrated that the decrease in the yield point at 15% strain for virgin hair may be as high as 45.1% after a total radiation dose of  $3.52 \cdot 10^4$  langleys (approximately a 2-month exposure to sunlight in summer). Bleach-modified hair underwent similar damage, with the yield point declining by 36.1% after a total radiation dose of  $3.31 \cdot 10^4$  langleys. The change in the yield point at 15% strain was found to be linear with the logarithm of the dose in the range of  $1-4 \cdot 10^4$  langleys. The deterioration in the tensile properties of hair were of the same magnitude in artificial-UV irradiation experiments.

#### EXPOSURE TO SOLVENTS, DETERGENTS, AND OTHER CHEMICALS—SUPERCONTRACTION

Solvents can alter the physical properties of hair by extracting materials which play a structural role, or by interacting with the macromolecular components to induce conformational changes to a more stable energetic form. Although commercially available hair-care products are based on water, lower alcohols (ethanol or isopropanol), and their mixtures, interaction of hair with other solvents was also investigated. Humphries *et al.* (21) studied the effect of diethyl ether, hexane, methanol, ethanol, and chloroform on

the thermal properties of hair. Transformations in the solvent-exposed hair were not observed in DTA or TGA experiments, while TMA was found to be sensitive to alterations. In general, the solvents reduced the temperature of the first transverse penetration (at 59°C for untreated hair) by 15°C. Diethyl ether was the only solvent that increased the 256°C expansion from 54% to 102%. In stress-strain measurements, 10–15% reduction in work to 25% extension was observed for water solutions containing 45–55% methanol, ethanol, or n-propanol (54,55). However, the weakening effect of alcohol-water mixtures is reversible, and resoaking the fibers in pure water nearly restores the original tensile properties.

Supercontraction (the term referring to the phenomenon of contraction of stretched or unstretched fibers subjected to certain chemical or physical treatments), usually performed by prolonged treatment of keratin fibers with 8M LiBr, causes a longitudinal shortening of the fibers (10–30%). An increase in fiber diameter (100%), as well as loss of the X-ray diffraction pattern and birefringence (2), also occurs. The supercontracted samples were reported to behave similarly to crosslinked samples in that some of the thermal transitions were shifted towards higher temperatures (21). Helix disruption can also be produced by exposure of hair (11) or wool (56) to perfluorooctanoic acid (PFO). The data obtained with human hair treated with PFO indicate a marked change of slope of the yield region and disappearance of the second-order phase transition.

Although anionic detergents such as sodium dodecyl sulfate interact with globular proteins or keratin fibers such as wool (57), they affect the mechanical properties of hair only to a slight extent (13). This is believed to be mainly due to the protective role of the cuticle, which acts as a diffusion barrier for the penetration of surfactants into the cortex. In contrast to this, fibers with cuticle removed by mechanical abrasion and saturated with SDS showed an increase of 35% in the average elastic modulus and about 50% in the loss modulus (13). It was postulated that the hydrophilic head of the SDS molecule reacts with polar side-chain groups, particularly in the microfibril areas, and the hydrophobic tail portion of the molecule sticks into the amorphous and more hydrophobic-like cortex. Consequently, SDS forms a quasi-salt bridge which is stronger than those present in the untreated fiber and also, because of its hydrophobicity in the tail section, drives water from the structure, leading to lower moisture regains at a given RH. Both of these effects increase  $E'$ . The marked increase in the loss modulus was ascribed to a disruption of the matrix by the non-polar parts of the SDS molecule.

Chlorine solutions have an adverse effect on the appearance and tactile properties of hair (17). The literature on chlorination of wool suggests a variety of degradative reaction pathways, including cystine rupture and oxidation, tyrosine degradation, peptide cleavage, and loss of protein substance during treatment (58–63). The reduction in the protein crosslink density leads to softening of the fiber surface. A systematic study of chlorination of hair was made by measuring inter-fiber friction by the twist method and SEM (17). Both "tip-to-root" and "root-to-tip" static and kinematic frictional coefficients increase as a function of the number of treatment cycles (in the range of 0–60 one-hour cycles) and chlorine concentration (in the range of 0–60 ppm). The rate of damage is considerably higher at low pH. At low pH the "tip-to-root" frictional coefficient may rise from 0.181 to as high as 0.347. In general, the changes in the frictional coefficient were greater in the case of measurements in the "root-to-tip" direction. The examination of surface morphology of friction-tested samples by SEM reveals that the

fiber surfaces gradually lose scale definition in the areas in which the fibers actually rubbed against each other after the chlorine test.

### ATTEMPTS TO REPAIR DAMAGE

As can be judged from the above-presented review of the physicochemical properties of hair subjected to a variety of cosmetic treatments, all of them, especially bleaching and relaxing, modify the original properties of keratin fibers. Cuticle destruction or removal, increased swelling, and brittleness are among the factors adversely affecting the appearance and tactile attributes of hair. Therefore, a substantial amount of work has been done to explore the means of protecting hair against the degradative action of weathering and handling or to restoring its original mechanical or surface properties after degradation. Preservation is achieved primarily by the use of conditioners which reduce the cuticle damage by decreasing frictional forces accompanying handling procedures. Although no method of practical utility was found to repair mechanically weakened hair, the general research strategy was to impart or to restore the conformational stability and mechanical integrity which in intact fibers is primarily derived from covalent crosslinking by cystine, interchain hydrogen bonding, electrostatic interactions, and, to a small extent, by hydrophobic bonding between nonpolar residues. Basically three approaches were utilized:

#### 1. TREATING HAIR WITH LOW-MOLECULAR-WEIGHT COMPOUNDS CAPABLE OF REACTING WITH KERATIN PROTEIN AND PRODUCING CROSSLINKING OR A HYDROPHOBIC EFFECT

A technique of hair treatment involving the introduction of nonpolar residues into the hair structure has been reported (64). This work was based on an earlier report (65) that the wet mechanical properties of reduced keratin fibers could be restored without crosslinking by incorporating high-molecular-weight alkylmonohalides into the fiber structure. Successful mechanical recovery of the alkylated fibers was attributed to hydrophobic interactions between alkyl moieties. For hair, S-alkylation with alkyl halides did not produce the expected increase in the 30% extension work index. On the other hand, the use of N-alkylmaleimides, standard blocking agents for protein sulfhydryl, proved to be an efficient way to reduce water swellability (from 39.9 to 28.2% in the case of treatment with N-dodecyl maleimide) and increase the wet-yield stress (from 0.22 to 0.32 g/denier) of reduced fibers.

Qualitatively similar effects can be achieved by introducing other bulky, hydrophobic groups into keratin. Phenyl isocyanate, which reacts with the amino, carboxyl, and thiol groups of keratin, and ninhydrin, which forms Ruhemann's purple with amino groups, both produce a dramatic increase in  $W_{20}$  in the temperature range of 0–25°C (11). The  $H_{20}$  was also altered markedly at low temperatures (0–25°C), decreasing from 0.524 (measured at 25°C) for untreated hair to 0.267 for ninhydrin-treated hair and 0.157 for isocyanate-treated hair. At higher temperatures the  $H_{20}$  approached the value of the control fibers. All these changes were interpreted by assuming a reduction in water content and thus increased viscosity of the keratin protein.

Formaldehyde is reactive with many of the functional groups on the peptide backbone (primary amino groups, tyrosyl and tryptophane residues (66,67)) and is able to react with groups containing active hydrogens to form methylene bridges (crosslinks) be-

tween protein chains. Exposure of hair fibers to formaldehyde vapor resulted in 20°C upscale shifts in low and high temperature transitions as detected by TMA and DTA (21). The stiffening of formaldehyde-treated hair is also reflected in a small increase of  $W_{20}$  from 350 to 389 at 25°C (11). The plot of the hysteresis ratio versus temperature for formaldehyde-treated fibers showed no change from that of control fibers. Feughelman and Watt also observed only a moderate increase in the viscosity ratio (wet/dry) in torsional measurements of formaldehyde-modified wool (68).

## 2. POLYMERIZATION OR POLYCONDENSATION OF MONOMERS WITHIN THE KERATIN FIBERS

Pioneering work on the deposition of polymers inside the structure of keratin fibers was done by Speakman (69,70). The field has been extensively explored in recent years, especially in relation to wool fibers, and the use of a variety of monomers, initiating systems, and solvents has been described. Several reviews and a large number of papers are available on this subject (71).

Table I lists examples of systems applied for graft copolymerization or polymer deposition in hair. It was established that the process of deposition is diffusion-controlled (73) and, consequently, to enhance the accessibility of the fiber to initiators and monomers the first step of the modification procedure is the reduction of cystine crosslinks (72). This is especially important in the case of hair keratin, where the high density of cystine crosslinks considerably impedes the diffusion of reagents. Reduction is usually performed by the use of thioglycolic acid (73–75), bisulfite, or tetrakis(hydroxymethyl)phosphonium chloride (72), which can also act as an effective oxygen scavenger in persulfate-initiated vinyl polymerizations. Under acidic conditions, tris(hydroxymethyl)phosphine, the product of THPC dissociation, reacts readily with hydrogen peroxide or dissolved oxygen but was reported to be inert towards persulfates. Disulfide reduction produces two cysteine residues which can be utilized to form a redox couple with suitable oxidizing agents such as the persulfate ion. A further advantage of THPC is that this reagent, unlike bisulfite or TGA, should not interfere with the process of initiation by the formation of a redox system. For polymerizing into bleached hair, the amount of graft copolymer increases with the degree of bleaching. Since bleaching destroys crosslinks inside the hair, it opens up the hair structure, and the enhanced diffusion augments the overall grafting yield (76,80).

Only a limited amount of monomers and initiating systems have been tested in graft copolymerizations involving hair fibers (Table I). Methacrylamide, salts of acrylic and methacrylic acid, were shown to be deposited with excellent yield (20–80% add-on) without appreciable, undesired modification of the fiber surface properties (72,76,77). Nonionic N-ethylmethacrylamide and N-vinylpyrrolidone, as well as cationic methacrylamidopropyltrimethylammonium chloride, were shown to produce only modest gains (4–5%) in fiber weight (83). Contradictory reports exist on the deposition of amine-containing monomers N,N-dimethylaminoethylmethacrylate and N,N-dimethylaminopropylmethacrylamide. The former was shown to produce 20.9% add-ons (74,75), while the latter formed only 4–8% deposits in reduced fibers (83). It was suggested that both steric and electrostatic factors might determine the rate and extent of the deposition, although this interpretation does not find consistent support in the existing data (83). Application of an aqueous solution containing an oligomeric precondensate of glyceraldehyde and resorcinol, under conditions promoting *in situ* polycon-

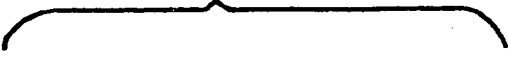
Table I  
Some Examples of Systems for Graft Copolymerization or Polymer Deposition in Hair

Monomer	Solvent	Pretreatment	Initiator	Extent of grafting or deposition	Properties of modified fibers	Ref.
Methacrylamide	H <sub>2</sub> O	0.2 M THPC in acetate buffer at 40°C for 30 min	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Up to 85% deposit	Not reported	72
Methyl methacrylate	H <sub>2</sub> O-EtOH (60:40)	6% Ammonium thioglycolate at pH 9.2 for 10 min	Cumene hydroperoxide	Up to 30% add-on		
		5% Sodium bisulfite in 45% EtOH for 10 min	Cumene hydroperoxide	Up to 30% add-on	Fiber surface heavily coated with the polymer at high % add-on	73
		Bleached hair	Cumene hydroperoxide	Up to 38% add-on proportional to the extent of bleaching		
		Reduced-oxidized hair	Cumene hydroperoxide	Up to 116% add-on		
N,N-dimethylaminoethyl methacrylate	H <sub>2</sub> O-EtOH	6% Ammonium thioglycolate at pH 9 for 5 min	Cumene hydroperoxide	20.9% Add-on	Wet load extension properties unaffected. Increased rate of sorption and sorption capacity for anionic dyes; 16% increase in work to 20% extension in the wet state after treatment with Hg <sup>++</sup>	74, 75

Methacrylic acid	H <sub>2</sub> O-EtOH	6% Ammonium thioglycolate at pH 9 for 5 min	Cumene hydroperoxide	37% Add-on	Increased rate of sorption and sorption capacity for metal ions; 4.9% increase in work to 20% extension in the wet state after treatment with NiCl <sub>2</sub> , Cu(OAc) <sub>2</sub> , Hg(OAc) <sub>2</sub>	74, 75
Ethylene glycol mono-methacrylate	H <sub>2</sub> O-EtOH	6% Ammonium thioglycolate at pH 9 for 5 min	Cumene hydroperoxide	21% Add-on	23% Increase in work to 20% extension in the wet state after treatment with Hg <sup>+2</sup>	74
Acrylonitrile	H <sub>2</sub> O-EtOH	6% Ammonium thioglycolate at pH 9 for 5 min	Cumene hydroperoxide	12%	48% Increase in the work to 20% extension in the wet state after treatment with Hg <sup>+2</sup>	74
Formaldehyde-resorcinol precondensate	H <sub>2</sub> O	2% Thioglycolic acid at pH 8; Reduction decreases E' and E'' to (3.5 ± 0.2) · 10 <sup>11</sup> pascals and (0.17 ± 0.02) · 10 <sup>11</sup> pascals, respectively	Not reported	5.2% 9.2% 21.5%	E' (pascals) 3.7 · 10 <sup>11</sup> 3.8 · 10 <sup>11</sup> 3.8 · 10 <sup>11</sup> E'' (pascals) 0.24 · 10 <sup>11</sup> 0.27 · 10 <sup>11</sup> 0.28 · 10 <sup>11</sup>	13
Na, K acrylate Patent covers acrylic acid, methacrylic acid, itaconic acid, and their salts and polymers	H <sub>2</sub> O	Bleaching by treatment with H <sub>2</sub> O <sub>2</sub> /K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> /CaCl <sub>2</sub>	Not reported	Up to 50% increase in tensile modulus as compared to bleach-only samples	76, 77

Table I (continued)

Monomer	Solvent	Pretreatment	Initiator	Extent of grafting or deposition	Properties of modified fibers	Ref.
Methyl methacrylate (patent covers the whole range of vinyl monomers)	H <sub>2</sub> O-ethylene glycol monomethyl ether	Reduction	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> /LiBr	Up to 33% add-on	Moisture repellency of hair increased	78
Na acrylate and methacrylate (support work for 74,75)	H <sub>2</sub> O	Bleaching	NaHSO <sub>3</sub> / (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Not reported	Strengthening of fibers by measurements of force at 15% extension and force at breakpoint; F <sub>15</sub> for dry fibers increased from 36.3 to 45.9 G; F <sub>15</sub> for wet fibers increased from 59.4 to 79.8 G; For wet fibers a decrease of F <sub>15</sub> in relation to untreated hair was observed	79
Methacrylamide	H <sub>2</sub> O	No pretreatment or bleached hair	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> NaBr pH 6.4	For bleached and untreated hair up to 16% add-on; Rate of deposition faster for bleached hair.	Cross-section area increased by 5-10% for untreated and 6-18% for bleached hair; Dry F <sub>15</sub> , tensile strength, Young's modulus, wet F <sub>15</sub> increased after deposition; Wet and dry combability negatively affected; 45-65% split ends mended	80
Resorcinol-alkylheximinium salts	H <sub>2</sub> O	Untreated, or reduced, or bleached hair	pH 4-7	5-15% Add-on for untreated hair	% Water uptake at 65% RH reduced from 13.5 to 7-12.5%; Deleterious modification of fiber surface at high polymer uptakes	81

Precon- densate glycerol- dehyde- resorcinol	H <sub>2</sub> O	Untreated hair	Boric, silicic, citric acids	Not reported	Curl retention improved by 80- 200%	82
N-methyl methacryl- amide				10.7% Add-on		83
N-methyl acrylamide				12.4% Add-on		
N-ethyl methacryl- amide	H <sub>2</sub> O	THPC reduction	H <sub>2</sub> O <sub>2</sub>	4.6% Add-on		
N-vinyl- pyrrolidone				4.4% Add-on		
MAPTAC				4.5-8% Add-on		
dimethyl- aminopropyl methacryl- amide				4.5-8% Add-on	No Surface coating; Other properties not reported	

MAPTAC-methacrylamidopropyltrimethylammonium chloride.



densation, is claimed to produce polymer deposits that improve hair settability, although no numerical data regarding the extent of grafting were quoted (82). The low-molecular-weight system comprising resorcinol and heximinium salts impregnates untreated hair, resulting in 5–15% add-ons which reduce fiber moisture uptake by a few percent (81).

Peroxides or hydroperoxides were found to be particularly effective as initiators for vinyl polymerization, mainly due to the formation of redox couples with thiol groups (72–80). Analysis of the literature on grafting of vinyl monomers on wool reveals the successful application of both chemical and radiation methods of initiation (71). Transition and non-transition metal ions in their higher valence states have also been used as initiators (71).

Generally, deposition of synthetic polymers results in small changes in the mechanical properties of hair. The process of reduction results in weakening of the fibers, as reflected by the measurements of the wet extension properties (about 15% decrease in work to 20% extension, elastic limit, or force to elastic limit after mild TGA reduction), and impregnation with polymers affords insignificant recovery of the tensile properties (75). Only for heavily weakened fibers, after extensive bleaching, considerable increase in tensile modulus was reported (77). In contrast to this, remarkable enhancement of the mechanical properties of reduced and bleached hair was noted after polymerizing vinyl monomers within the fiber and subsequently reacting them with metal salts (75). Improvement of wet-load extension properties in the range of 16–48% was observed after the deposition of poly(dimethylaminoethylmethacrylate) (PDEM), polyacrylonitrile, or poly(ethylene glycol monomethacrylate), followed by the complexation with mercuric acetate. Relatively small effects were brought out by the same treatment to carboxylic acid-containing hair. The amelioration in the wet-load extension properties of PDEM-containing hair appears to be related to the amount of synthetic polymer in the fibers. Other metals, e.g., Cu(II) and Ni(II) were found to produce similar, albeit smaller effects.

An increase in cross-sectional area (80), split-end mending (80), water sorption reduction, and improvement of the curl retention (81,82) are quoted as advantages for hair fiber modification by polymer deposition. These are, however, sometimes offset by deleterious coating of the fiber surface, negatively affecting both dry and wet combability, especially at high polymer uptakes (80).

### 3. SURFACE POLYMERIZATION AND DIRECT APPLICATION OF SURFACE POLYMER FILMS

Interfacial polymerization can be used to deposit linear polyamides, polyurethanes, or polyureas on the surface of wool fibers (84). The modification protocol calls for impregnating wool with an aqueous solution of diamine and then immersing it in a solution of a diacyl chloride, bischloroformate, or diisocyanate in an inert organic solvent. This procedure results in the formation of polymer at the boundary of the solvents, that is, at the fiber surface. In an alternative process, pre-formed polymers are applied directly to the fiber surface to form a shrink-resistant coating. These polymer systems usually contain reactive groups such as carboxylic acid chloride, azetidinium, thiol, isocyanate, carbamoylsulfonate, N-methylolamide, or silanol, which can form both polymer-polymer or polymer-fiber crosslinks.

In the case of hair, most of these procedures or compositions are not functional since they unacceptably refashion the fiber surface. One viable route avoiding deleterious alterations of the fiber surface was delineated in the patent literature (85). It involves the treatment of weakened hair with reactive silanes such as alkyltrialkoxysilanes in the presence of alcohol and water (0–20%). A preliminary account of silylation with hexamethyldisilazane was also reported to enhance the stability of straightened hair (86). Reactive trialkoxysilane hydrolyzes in the presence of water to form reactive silanol groups which in turn condense with each other or with the reactive groups on the fiber surface to form a polymeric coating. The process of application is completed by blow drying the hair with hot air. Tensile strength (the force required to break hair) and silicon content in hair were ascertained for hair samples damaged in the process of relaxation by alkali and reducing agents. Control virgin hair is characterized by a tensile strength of  $29.5 \pm 0.6$  G/cross-section, and for alkali-damaged hair this value decreases to  $14.5 \pm 1.1$  G/cross-section. The data exemplified in the patent show a 15–20% increase in the tensile strength of alkali-damaged hair samples after treatment with ethyltriethoxysilane to the value of  $14.5\text{--}17 \pm 0.7$  G/cross-section. It was also claimed that treatment with octadecyltrimethoxysilane, 3-aminopropyltriethoxysilane, vinyltriethoxysilane, and N-(triethoxysilylpropyl)urea imparted good settability and curl retention to damaged hair tresses even after post-treatment shampooings.

## CONCLUSIONS

Owing to its unique composition and structure, human hair displays greater resistance to mechanical damage while dry than in the wet state. Structural integrity is derived mainly from the high density of disulfide bridges between cystine components of the protein. Rupture of these crosslinks, attained in cosmetic treatments by reaction with mercaptans, alkalis, or oxidation by hydrogen peroxide leads to weakening of the wet fibers. Matrix-dependent properties such as the torsional modulus, moisture sorption, and swelling are affected to a larger extent than microfibril-determined, longitudinal characteristics. Environmental agents, such as UV irradiation, also contribute to a gradual loss of the original fiber strength and cohesion. Except for reduction with mercaptans, which can be partially remedied by reoxidation, inflicted damage is irreversible and results in increased swelling, brittleness, and susceptibility to destruction, even during normal handling operations. Surface despoliation, by mechanical abrasion in the wet state or by the chemical action of chlorine, bleaching, or dyeing compositions, is an important aspect of hair destruction, resulting in an increase in frictional coefficients and, consequently, combing forces.

Efforts to restore the original properties of hair after mild degradation or to protect undamaged hair against structural weakening have been numerous but largely unsuccessful. Severely impaired structure, such as from bleaching or relaxation, is probably easier to mend in the sense that any improvement in strength or swellability should be more perceptible in terms of tactile properties, manageability, or settability. Polymer deposition or grafting, in spite of its limitations and side effects such as surface modification, still has some potential in this respect, provided that new monomer or initiating systems are discovered.

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**United States Patent** [19]

Anderson et al.

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[54] **OXIDATIVE HAIR DYE COMPOSITIONS  
AND METHODS CONTAINING 1-(4-  
AMINOPHENYL) PYRROLIDINES**

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8/412; 8/423; 8/574**

[58] **Field of Search** ..... **8/406, 408, 409,  
8/410, 411, 412, 416, 423, 574; 548/577,  
579**

[56] **References Cited**

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[57] **ABSTRACT**

The invention provides compositions and methods for the oxidative coloring of human hair. The compositions of the invention contain as a primary dye intermediate a 1-(4-aminophenyl) pyrrolidine, or a cosmetically acceptable salt thereof. The compositions may also contain at least one other primary intermediate and conventional coupling compounds, in addition to an oxidizing agent and other components typically used in oxidative hair dye preparations. Preferred dye intermediates in the compositions of the invention include 1-(4-aminophenyl) pyrrolidine and 1-(4-amino-3-methylphenyl) pyrrolidine, or cosmetically acceptable salts thereof, which produce intense neutral colors when used in admixture with a suitable coupling agents, such as 3-aminophenol, in conventional hair dye base formulations.

**30 Claims, No Drawings**

# OXIDATIVE HAIR DYE COMPOSITIONS AND METHODS CONTAINING 1-(4-AMINOPHENYL) PYRROLIDINES

## FIELD OF THE INVENTION

The invention relates generally to methods and compositions for preparing stable oxidative hair dyes that result in long-lasting and true color and do not adversely affect the texture and condition of the hair after application. The present invention more particularly relates to oxidative hair dye compositions and methods comprising 1-(4-aminophenyl) pyrrolidines, as primary intermediates, in addition to other conventionally-used additives and components.

## BACKGROUND OF THE INVENTION

Oxidative hair dye colorants are essential elements in hair dyeing preparations for the permanent dyeing of human hair. The hair dyeing process is achieved, in general, by the reaction of certain developing compounds with certain coupling compounds in the presence of a suitable oxidizing agent or compound, such as hydrogen peroxide.

When oxidation dyes, such as those comprising primary intermediates, and couplers are used in the dyeing of human hair, the procedure may involve the use of a two part system. In general, one part can be a lotion formulation which contains a variety of ingredients, including oxidation dye precursors (i.e., primary intermediates and coupling agents). The other part is a developer formulation containing a suitable oxidizing agent, e.g., hydrogen peroxide. Immediately prior to application to the hair, the two parts are mixed to form a thickened liquid solution, for example, a lotion or a gel. As a consequence of the oxidizing properties of the oxidizing agent, some of the natural melanin pigment of the hair may be bleached. The precursors in the thickened solution (e.g., lotion or gel) penetrate into the hair and are oxidized to produce the desired color. Such systems generally contain a proportion of organic solvents and surfactants and contain relatively high levels of dye precursors to produce the desired color.

In order for procedures using permanent oxidative dyes to work properly, a number of parameters and conditions are important to consider in the use of these dyes in admixture with couplers in hair color preparations for human hair. Among these are the final color and color intensity that are produced after application to the subject's hair; the wash fastness and the light fastness of the resulting dye; the resistance of the dye to perspiration; the type of hair being dyed, e.g., virgin hair or waved hair; the resistance of the dye to various hair treatments, such as permanent wave, straightening, shampooing, conditioning and rubbing. In addition, the dye must have virtually no allergenicity or dermal or systemic toxicity.

1,4-benzenediamine (i.e., para-phenylenediamine or PPD) is a primary intermediate widely used in oxidative hair dye compositions. When coupled with a conventional coupling agent, such as 3-aminophenol, it forms a unique color which is very intense in depth, yet neutral in shade. However, PPD is known to be both an allergen and a sensitizer. Therefore, needed in the art are primary intermediates that are capable of forming the unique color and shade performance of PPD, but which are more toxicologically benign. Such new primary intermediates can be used to replace PPD or used in conjunction with PPD, in whole or in part.

Until the present invention, no primary dye intermediate has been found as a dye component, which generates a

quality of color that is comparable or equivalent to that produced by PPD when used with coupling substances as color modifiers. In addition, no primary dye intermediate, as a supplement or replacement for PPD, has to date been found which satisfies the above-listed requirements for oxidative colorants used in the dyeing of human hair.

U.S. Pat. No. 4,840,639 to H. Husemeyer et al. discloses hydroxyalkyl-substituted PPDs, namely, the 1-hydroxyalkyl-2,5-diaminobenzenes, such as 2-(2-hydroxyethyl) PPD, as a developing agent in oxidative hair dyes. GB 1,025,916 to L'Oréal discloses compounds such as 1-(4-aminophenyl) piperidine or 4-(4-aminophenyl) morpholine, and couplers, in hair dye compositions and methods.

The electrochemical, photographic, allergenic and coupling properties of 1-(4-aminophenyl) pyrrolidine is disclosed by R. L. Bent et al., *J. Am. Chem. Soc.*, 73:3100-3125, 1951 (Kodak Research Labs), in a long list of p-amino-N-allylaniline compounds used in color photographic processes (Table I of Bent et al.). The report of Bent et al. is strictly germane to the photographic arts and does not teach or contemplate the use of primary dye intermediates in the oxidative coloring of hair. Similarly, L. K. J. Tong et al., *J. Am. Chem. Soc.*, 82:1988-1996, 1959 (Kodak Research Labs), report the deamination of oxidized derivatives of p-phenylenediamines (Table I of Tong et al.). The studies of Tong et al. were carried out, in an unrelated field of art, in an effort to understand the mechanism of dye formation in connection with photographic image production.

The compounds of the present invention, which are of the class of 1-(4-aminophenyl) pyrrolidines, or cosmetically acceptable salts thereof, are clearly distinct from photographic and hair dyeing compounds disclosed in the prior art and offer newly-discovered and advantageous hair coloring properties.

## SUMMARY OF THE INVENTION

It is an object of the invention to provide oxidative hair dye compositions and methods comprising compounds of the class of 1-(4-aminophenyl) pyrrolidines, or cosmetically acceptable salts thereof, as primary intermediates in compositions comprising such primary dye intermediates as well as coupling agents, oxidizing agents and other adjuvant substances. In accordance with a particular aspect of the invention 1-(4-aminophenyl) pyrrolidine is preferred.

It is yet another object of the invention to provide compositions and methods for the oxidative coloration of hair comprising one or more novel primary dye intermediate compounds of the 1-(4-aminophenyl) pyrrolidine class of compounds, this class being toxicologically benign to the user.

It is a further object of the invention to provide 1-(4-aminophenyl) pyrrolidine compounds that serve as effective and high-performance primary intermediates in oxidative hair dyes. The 1-(4-aminophenyl) pyrrolidine compounds of the invention are capable of replacing, in whole or in part, paraphenylenediamine (PPD), a known allergen and a sensitizer, employed with couplers as color modifiers in such hair dye formulations.

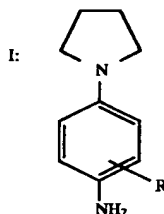
Yet another object of the invention is to provide a newly-discovered primary dye intermediate, 1-(4-amino-3-methylphenyl) pyrrolidine, or a cosmetically acceptable salt thereof, which provides intense color when used in oxidative hair dye compositions in combination with coupling agents, oxidizing agents and other hair dye additives and/or adjuvants conventionally used in hair dye formulations for the dyeing of hair.

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Further objects and advantages afforded by the invention will be apparent from the detailed description hereinbelow.

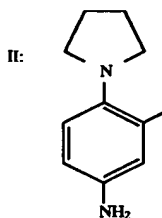
# DETAILED DESCRIPTION OF THE INVENTION

The present invention provides novel compounds which are primary intermediates for use in oxidative hair dye compositions. The compositions of the present invention include, as primary dye intermediates, one or more components from the chemical class of substituted or unsubstituted 1-(4-aminophenyl) pyrrolidine compounds, and derivatives and cosmetically acceptable salts thereof. Nonlimiting examples of derivatives and salts of the 1-(4-aminophenyl) pyrrolidine compounds include sulfates, hydrochlorides, phosphates and the like, with sulfates being preferred. The 1-(4-aminophenyl) pyrrolidine compounds of the present invention are generally represented by the following chemical formula I:

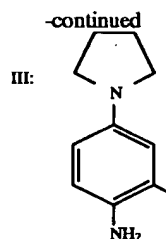


wherein R is a hydrogen (H) atom; C<sub>1</sub>-C<sub>6</sub> alkyl, preferably C<sub>1</sub>-C<sub>4</sub> alkyl more preferably C<sub>1</sub>-C<sub>2</sub> alkyl; or C<sub>1</sub>-C<sub>4</sub> mono- or polyhydroxyalkyl preferably C<sub>1</sub>-C<sub>3</sub> monohydroxyalkyl. Preferred are unsubstituted 1-(4-aminophenyl) pyrrolidine (e.g., formula I, wherein R is hydrogen), as well as substituted 1-(4-aminophenyl) pyrrolidines, (e.g., formula I, wherein R is methyl or ethyl).

In accordance with the present invention, substituted 1-(4-aminophenyl) pyrrolidines useful as primary dye intermediates in the hair coloring compositions of the invention include 1-(4-amino-2-methylphenyl) pyrrolidine and 1-(4-amino-3-methylphenyl) pyrrolidine or cosmetically acceptable salts thereof, for example, 1-(4-amino-2-methylphenyl) pyrrolidine sulfate and 1-(4-amino-3-methylphenyl) pyrrolidine sulfate, respectively. 1-(4-amino-2-methylphenyl) pyrrolidine and 1-(4-amino-3-methylphenyl) pyrrolidine have the structures depicted below as formulae II and III, respectively:

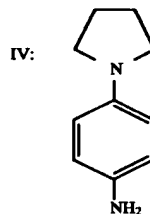


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Although compounds II and III are 1-(4-aminophenyl) pyrrolidines substituted with a methyl group, it was discovered that the placement of a methyl group at the 3 position of the phenyl ring resulted in a unique primary intermediate which afforded a deeper and richer shade of color to dyed hair and surprisingly exceeded the quite acceptable and useful coloring performance of the 4-aminophenyl pyrrolidine compound substituted with a methyl group at position 2 of the phenyl ring. Accordingly, both the substituted and unsubstituted 4-aminophenyl pyrrolidine compounds proved to be effective as primary dye intermediates with other hair dye components in oxidative hair dye compositions of the present invention.

A preferred unsubstituted 4-aminophenyl pyrrolidine compound of the present invention is 1-(4-aminophenyl) pyrrolidine, which is represented by the following formula IV:



The compositions of the present invention contain as a primary dye intermediate one or more substituted or unsubstituted 1-(4-aminophenyl) pyrrolidine compounds, or a cosmetically acceptable salt thereof, which may be present in admixture with one or more other dye component(s), for example, a primary dye intermediate, e.g., PPD, or conventional coupling component(s), in addition to other hair dye component ingredients, additives, or adjuvants typically used in oxidative hair dye formulations as described herein. The 1-(4-aminophenyl) pyrrolidines, alone or in combination with one or more other dye intermediates and coupling agents produce novel dyestuffs which provide intense coloration to hair. The 1-(4-aminophenyl) pyrrolidine compounds of the present invention achieve a deep coloration to hair and impart unique properties to dye substances used for oxidative hair coloring.

It will be appreciated by those having skill in the art that the compositions and methods of the present invention are appropriate for the dyeing of keratinous fibers, including the hair fibers of animals and humans, with particular application to the oxidative coloring of human hair.

In accordance with the present invention, members of the class of 1-(4-aminophenyl) pyrrolidine primary dye intermediate compounds have been discovered to be similar in coloring capacity to the conventionally-used primary intermediate PPD, i.e., to exhibit the same color and intensity when used in an oxidative hair dye product with a coupling compound as color modifier in hair dye formulations (Table 4).



The 1-(4-aminophenyl) pyrrolidines of the present invention and their cosmetically acceptable derivatives or salts afford particularly significant advantages as primary intermediates in dye compositions. These compounds can be used as substitutes for PPD and to replace PPD, in whole or in part, in dye compositions. For example, the compositions of the present invention formulated to contain 1-(4-aminophenyl) pyrrolidine, or a cosmetically acceptable derivative or salt thereof, for the oxidative dyeing of hair, afford outstanding effectiveness as colorants, with fewer adverse side effects than like compositions containing PPD. In addition, the present compositions satisfy the dermatological and toxicological requirements that should optimally be met by oxidative coloring substances, particularly for the coloring of human hair.

As described above, in addition to at least one of the novel component dye molecules encompassed by the present invention, the hair dyeing compositions described herein may also contain at least one other known and usual dye ingredient (i.e., used as primary dye intermediates and/or couplers), as well as conventional direct-acting colorants and dyes in admixture, should these substances be necessary or desired for the development and production of certain color nuances and tints.

Illustrative component dye ingredients that are conventionally admixed and employed as constituents of customary hair dye formulations and that can be considered suitable for use in the compositions of the present invention are set forth hereinbelow. As but one particular example, p-phenylenediamine, used in oxidative hair coloring formulations, may conveniently be used in admixture with the novel primary intermediate 1-(4-aminophenyl) pyrrolidine compounds in the compositions of the present invention.

Included among the suitable dye components that may be considered for use as primary intermediates and/or couplers in the dye compositions of the present invention are the following: p-phenylenediamine derivatives such as: p-toluenediamine; p-phenylenediamine; 2-chloro-p-phenylenediamine; N-phenyl-p-phenylenediamine; N-2-methoxyethyl-p-phenylenediamine; N,N-bis-hydroxyethyl-p-phenylenediamine; 2-hydroxymethyl-p-phenylenediamine; 2-hydroxyethyl-p-phenylenediamine; 4,4'-diaminodiphenylamine; 2,6-dimethyl-p-phenylenediamine; 2-isopropyl-p-phenylenediamine; N-(2-hydroxypropyl)-p-phenylenediamine; 2-propyl-p-phenylenediamine; 1,3-bis-(N-hydroxyethyl)-N-(4-aminophenyl)amino-2-propanol; and 2-methyl-4-dimethylaminoaniline, or combinations thereof.

Preferred p-phenylenediamine derivatives include: p-toluenediamine; p-phenylenediamine; N-2-methoxyethyl-p-phenylenediamine; N,N-bis-hydroxyethyl-p-phenylenediamine; and 2-hydroxyethyl-p-phenylenediamine.

p-Aminophenol derivatives include: p-aminophenol; p-methylaminophenol; 3-methyl-p-aminophenol; 2-hydroxymethyl-p-aminophenol; 2-methyl-p-aminophenol; 2-(2'-hydroxyethylaminomethyl)-p-aminophenol; 2-methoxymethyl-p-aminophenol; and 5-aminosalicylic acid, or combinations thereof.

Preferred p-aminophenol derivatives include: p-aminophenol; p-methylaminophenol; 3-methyl-p-aminophenol; 2-methyl-p-aminophenol; 2-(2'-hydroxyethylaminomethyl)-p-aminophenol; 2-methoxymethyl-p-aminophenol; and 5-aminosalicylic acid.

Ortho developers include: catechol; pyrogallol; o-aminophenol; 2,4-diaminophenol; 2,4,5-

trihydroxytoluene; 1,2,4-trihydroxybenzene; 2-ethylamino-p-cresol; 2,3-dihydroxynaphthalene; 5-methyl-o-aminophenol; 6-methyl-o-aminophenol; and 2-amino-5-acetaminophenol, or combinations thereof.

Preferred ortho developers include: o-aminophenol; 2,4-diaminophenol; 2,4,5-trihydroxytoluene; 1,2,4-trihydroxybenzene; 2-ethylamino-p-cresol; 5-methyl-o-aminophenol; 6-methyl-o-aminophenol; and 2-amino-5-acetaminophenol.

Phenols and resorcinol derivatives include: 2-methyl-1-naphthol; 1-acetoxy-2-methylnaphthalene; 1,7-dihydroxynaphthalene; resorcinol; 4-chlororesorcinol; 1-naphthol; 1,5-dihydroxynaphthalene; 2,7-dihydroxynaphthalene; hydroquinone; 2-methylresorcinol; 1-hydroxy-6-aminonaphthalene-3-sulfonic acid; thymol (2-isopropyl-5-methylphenol); 1,5-dihydroxy-1,2,3,4-tetrahydronaphthalene; 2-chlororesorcinol; 2,3-dihydroxy-1,4-naphthoquinone; and 1-naphthol-4-sulfonic acid, or combinations thereof.

Preferred phenols and resorcinol derivatives include: 2-methyl-1-naphthol; 1-acetoxy-2-methylnaphthalene; 1,7-dihydroxynaphthalene; resorcinol; 4-chlororesorcinol; 1-naphthol; 1,5-dihydroxynaphthalene; 2,7-dihydroxynaphthalene; hydroquinone; 2-methylresorcinol; thymol (2-isopropyl-5-methylphenol); and 2,3-dihydroxy-1,4-naphthoquinone.

m-Phenylenediamines include: m-phenylenediamine; 2-(2,4-diaminophenoxy)ethanol; N,N-(bis-hydroxyethyl) m-phenylenediamine; 2,6-diaminotoluene; N<sup>2</sup>-bis-hydroxyethyl-2,4-diaminophenetole; bis-(2,4-diaminophenoxy)-1,3-propane; hydroxyethyl-2,4-diaminobenzene; 2-amino-4-hydroxyethylamino anisole; aminoethoxy-2,4-diaminobenzene; 2,4-diaminophenoxyacetic acid; 4,6-(bis-hydroxyethoxy) m-phenylenediamine; 2,4-diamino-5-methylphenetole; 2,4-diamino-5-hydroxyethoxytoluene; 2,4-dimethoxy-1,3-diaminobenzene; and 2,6-(bis-hydroxyethylamino) toluene, or combinations thereof.

Preferred m-phenylenediamines include: m-phenylenediamine; 2,4-diaminophenoxyethanol; bis-(2,4-diaminophenoxy)-1,3-propane; hydroxyethyl-2,4-diaminobenzene; 2-amino-4-hydroxyethylamino anisole; 4,6-bis-hydroxyethoxy-m-phenylenediamine; 2,4-diamino-5-methylphenetole; 2,4-diamino-5-hydroxyethoxytoluene; 2,4-dimethoxy-1,3-diaminobenzene; and 2,6-(bis-hydroxyethylamino) toluene.

m-Aminophenols include: m-aminophenol; 2-hydroxy-4-carbamoylmethylamino toluene; m-carbamoylmethylamino phenol; 6-hydroxybenzomorpholine; 2-hydroxy-4-aminotoluene; 2-hydroxy-4-hydroxyethylaminotoluene; 4,6-dichloro-m-aminophenol; 2-methyl-m-aminophenol; 2-chloro-6-methyl-m-aminophenol; 2-hydroxyethoxy-5-aminophenol; 2-chloro-5-trifluoroethylaminophenol; 4-chloro-6-methyl-m-aminophenol; N-cyclopentyl-3-aminophenol; N-hydroxyethyl-4-methoxy-2-methyl-m-aminophenol and 5-amino-4-methoxy-2-methylphenol, or combinations thereof.

Preferred m-aminophenols include: m-aminophenol; 6-hydroxybenzomorpholine; 2-hydroxy-4-aminotoluene; 2-hydroxy-4-hydroxyethylaminotoluene; 4,6-dichloro-m-aminophenol; 2-methyl-m-aminophenol; 2-chloro-6-methyl-m-aminophenol; 4-chloro-6-methyl-m-aminophenol; N-cyclopentyl-3-aminophenol; N-hydroxyethyl-4-methoxy-2-methyl-m-aminophenol and 5-amino-4-methoxy-2-methylphenol.

Heterocyclic derivatives include: 2-dimethylamino-5-aminopyridine; 2,4,5,6-tetra-aminopyrimidine; 4,5-

diamino-1-methyl-pyrazole; 1-phenyl-3-methyl-5-pyrazolone; 6-methoxy-8-aminoquinoline; 2,6-dihydroxy-4-methylpyridine; 5-hydroxy-1,4-benzodioxane; 3,4-methylenedioxyphenol; 4-hydroxyethylamino-1,2-methylenedioxybenzene; 2,6-dihydroxy-3,4-dimethylpyridine; 5-chloro-2,3-dihydroxypyridine; 3,5-diamino-2,6-dimethoxypyridine; 2-hydroxyethylamino-6-methoxy-3-aminopyridine; 3,4-methylenedioxyaniline; 2,6-bis-hydroxyethyloxy-3,5-diaminopyridine; 4-hydroxyindole; 3-amino-5-hydroxy-2,6-dimethoxypyridine; 5,6-dihydroxyindole; 7-hydroxyindole; 5-hydroxyindole; 2-bromo-4,5-methylenedioxyphenol; 6-hydroxyindole; isatin (indole-2,3-dione); 3-amino-2-methylamino-6-methoxypyridine; 2-amino-3-hydroxypyridine; 2,6-diaminopyridine; 5-(3,5-diamino-2-pyridyloxy)-1,3-dihydroxypentane; 3-(3,5-diamino-2-pyridyloxy)-2-hydroxypropanol and 4-hydroxy-2,5,6-triaminopyrimidine, or combinations thereof.

Preferred heterocyclic derivatives include: 4,5-diamino-1-methyl-pyrazole; 2-dimethylamino-5-aminopyridine; 2,4,5,6-tetra-aminopyrimidine; 1-phenyl-3-methyl-5-pyrazolone; 3,4-methylenedioxyphenol; 4-hydroxyethylamino-1,2-methylenedioxybenzene; 2,6-dihydroxy-3,4-dimethylpyridine; 5-chloro-2,3-dihydroxypyridine; 3,5-diamino-2,6-dimethoxypyridine; 2-hydroxyethylamino-6-methoxy-3-aminopyridine; 3,4-methylenedioxyaniline; 4-hydroxyindole; 5,6-dihydroxyindole; 7-hydroxyindole; 5-hydroxyindole; 2-bromo-4,5-methylenedioxyphenol; 6-hydroxyindole; isatin (indole-2,3-dione); 3-amino-2-methylamino-6-methoxypyridine; 2-amino-3-hydroxypyridine; 2,6-diaminopyridine; 5-(3,5-diamino-2-pyridyloxy)-1,3-dihydroxypentane; 3-(3,5-diamino-2-pyridyloxy)-2-hydroxypropanol and 4-hydroxy-2,5,6-triaminopyrimidine.

The additional dye compounds, e.g., couplers, should be present in the hair dyeing compositions of the present invention in an amount of approximately 0.01 to 10%, by weight, preferably approximately 0.1 to 5%, by weight, based on the total weight of the composition. The total quantity of oxidative colorant, comprising dye substance(s) and coupling substance(s) will suitably amount to approximately 0.1 to 10%, by weight, and preferably, approximately 0.5 to 5% by weight, based on the total weight of the composition.

Unless indicated otherwise, as used herein, reagent or component amounts are in % by weight (w/w), based on the total weight of the composition.

In the compositions of the present invention, the coupling component is generally used in approximately equimolar amounts relative to the developing component. However, it will be appreciated that the dye component, in relation to the coupler, may be present either in increased or decreased amounts depending upon the formulation and the desired color, intensity or effect. In general terms, the dye component and the coupling component, or cosmetically acceptable salts thereof, will be present in tinctorially effective amounts for the coloring of a hair fiber.

The hair dye preparations of the present invention may be formulated into cosmetic preparations such as a solution, cream, lotion, gel or emulsion. Also, in accordance with the invention, the compositions may represent a mixture of the coloring components (i.e., dye intermediate and coupling agent) in with other components commonly associated with the formulation of solutions, creams, lotions, gels or emulsions, and the like. For example, components such as wetting agents or emulsifying agents from the categories of anionic or non-ionic surfactants, such as sulfates of fatty

alcohols, alkanolamides of fatty alcohols, alkyl sulfonates, alkylbenzene sulfonates, oxyethylated fatty alcohols, oxyethylated nonylphenols; furthermore thickeners such as fatty alcohols, starch, cellulose derivatives, paraffin oil and fatty acids, as well as hair-care substances such as lanolin derivatives, cholesterol and pantothenic acid, may be formulated into the compositions of the invention.

As an example, if formulated as a lotion, the compositions of the invention may contain organic solvents to assist in dissolving the dye precursors. Accordingly, the organic solvent content of the lotion may be from 0% to about 20%, preferably, about 1% to about 15%. Typically useful solvents include alcohols containing up to three carbon atoms such as ethanol and isopropanol, polyhydroxy alcohols such as propylene or hexylene glycol and lower alkyl ethers thereof, such as ethoxy ethers.

In addition, the hair dyeing compositions in accordance with the present invention may optionally contain conventionally-used adjuvants and cosmetic additives, or mixtures thereof, to achieve the final formulations. Examples of such additives include, but are not limited to, anti-oxidants, e.g., ascorbic acid, erythorbic acid, or sodium sulfite, to inhibit premature oxidizing; oxidizing agents; fragrances and/or perfume oils; chelating agents; emulsifiers; coloring agents; thickeners; organic solvents; opacifying agents; dispersing agents; sequestering agents; hair-care substances; humectants; and anti-microbials, and others. The list of optional ingredients is not intended as limiting. Other suitable adjuvants for inclusion in the hair dye compositions of the invention are disclosed, for example, in Zviak, *The Science of Hair Care* (1986) and in Balsam and Sagarin, *Cosmetics: Science and Technology*, Vol. 2, Second Edition, (1972).

More specifically, organic solvents used in the hair dye compositions assist in dissolving the dyes. Typically useful solvents include, but are not limited to, alcohols containing up to three carbon atoms, such as ethanol and isopropanol, as well as polyhydroxy alcohols, such as propylene glycol and hexylene glycol. Lower alkyl ethers, such as ethoxy diglycol may be used.

Thickeners that may be used in the compositions of the present invention include a variety of fatty acid soaps and associative polymeric thickeners. The fatty acid soaps are alkaline metal salts or alkanolamine salts of fatty acids with C<sub>10</sub>-C<sub>16</sub> alkyl side chains. The preferred fatty acids include oleic acid, myristic acid and lauric acid, which are generally present in the compositions of the invention at about 0.5% to about 20%, preferably about 1% to about 10%. Associative thickeners are polymers that can thicken solutions at low concentrations. Among the associative thickeners that are useful in the compositions of the present invention are acrylates copolymer (sold by Rohm and Haas under the tradename Aculyn-33), cetareth-20 acrylates/steareth-20 methacrylate copolymer (sold by Rohm and Haas under the Trade Name Aculyn-22), acrylates/steareth-20 itaconate copolymer and acrylates/ceteth-20 itaconate copolymer. Another class of associative thickeners that is useful in the compositions of the present invention include the copolymers of polyurethane and polyethylene glycol or polyether urethanes. One such material is sold by Rohm and Haas under the tradename Aculyn-44. The associative polymeric thickeners are generally present in the compositions of the invention at about 0.1% to about 10%, preferably, about 0.5% to about 5%.

The oxidative coupling, i.e., the development of the dye, to produce the final color product on the hair, can, in principle, be performed with atmospheric oxygen. However,

chemical oxidizing agents are suitably and preferably used. Although other oxidizing agents can be employed, hydrogen peroxide is a preferred oxidizing compound for use as a developer with the primary intermediate and coupler dye precursors of the invention. The concentration of hydrogen peroxide in the developer may be from about 1% to about 15%, preferably, from about 3% to about 12%. Other suitable oxidizing agents include, for example, urea peroxide, melamine peroxide, perborates and percarbonates such as sodium perborate or percarbonate. The amounts of such oxidizing agents can be routinely determined by one having skill in the art, without requiring any inventive skill.

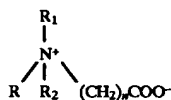
The compositions of the invention may include a typical anionic, cationic, nonionic or amphoteric surfactant. The anionic surfactants include the variety of alkyl sulfates, alkylether sulfates, alkyl sulfonates, alkyl sulfosuccinates and N-acyl sarcosinates. The commonly-used anionic surfactants are sodium and ammonium lauryl sulfates, sodium and ammonium laureth sulfate and alpha olefin sulfonates. Anionic surfactants are generally present in the compositions of the present invention at about 0.1% to about 15%, preferably, about 0.5% to about 10%.

The nonionic surfactants that can be used in the present invention include the wide variety of ethoxylated alcohols, nonoxynols, alkanolamides, alkyl stearates, alkyl palmitates and alkylpolyglucosides. Examples of the commonly-used nonionic surfactants are cetyl alcohol, stearyl alcohol, oleyl alcohol; the various types of ethoxylated alkylphenols; lauramide diethanolamide (DEA); lauramide monoethanolamide (MEA); isopropyl palmitate, isopropyl stearate and decylpolyglucoside. Nonionic surfactants are generally present in the compositions of the present invention at about 0.1% to about 15%, preferably, about 0.5% to about 10%.

The compositions in accordance with the present invention may also contain one or more quaternary ammonium compounds that provide hair conditioning effects. The quaternary ammonium compounds can be monomeric or polymeric quaternary ammonium compounds. Nonlimiting examples of such compounds include cetyltrimonium chloride, stearyl trimonium chloride, benzalkonium chloride, behentrimonium chloride and a variety of polyquaterniums. The quaternary ammonium compounds are generally present in the compositions of the present invention at about 0.1% to about 10%, preferably, about 0.5% to about 5%.

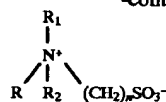
Amphoteric surfactants that can be incorporated in the compositions of the present invention belong to the class of surface active chemicals that possess a positive and a negative charge in the same molecule and behave as a cation, an anion, or both, depending upon the pH of the medium and the nature of the amphoteric molecule. In general, the positive charge is located on a nitrogen, while the negative charge is carried by a carboxyl or sulfonate group. There are a large number of amphoteric surfactants that are suitable for use in the present invention, including, for example, the well-known betaines, sultaines, glycinate and propionates that may generally be represented by the following structural formulae shown below:

1. Betaines:

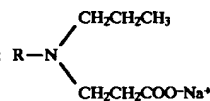


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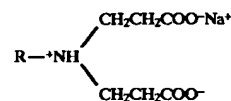
2. Sultaines:



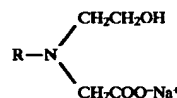
3. Propionates:



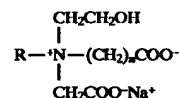
or



4. Glycinates:



or



In these formulae, R is an alkyl or alkylamide group containing from about 10 to about 20 carbon atoms. R<sub>1</sub> and R<sub>2</sub> are alkyl or hydroxyalkyl groups, which may be the same or different, and contain up to about five carbon atoms; n is a positive integer from one to about five.

The selection of the amphoteric surfactant or mixture of surfactants for use in the present compositions and methods is not critical. The surfactant may be selected from among those suggested above, or from any of a number of other known amphoteric surfactants. The amount of amphoteric surfactant in the compositions of the present invention is normally from about 0.5% to about 15%, preferably, about 2% to about 10%.

Depending on the final formulated preparation, the compositions in accordance with invention may be weakly acidic, neutral or alkaline. In particular, the pH of the prepared compositions can range from about 5 to about 11. Preferred is a pH range of about 8 to 10. Any of a wide variety of alkaline reagents can be used to adjust the pH of the hair coloring compositions. Such alkaline reagents include ammonium hydroxide, potassium or calcium hydroxide, sodium or potassium carbonate, sodium phosphate, sodium silicate, guanidine hydroxide, or any one of the alkylamines or alkanolamines, for example, ethylamine, triethylamine, trihydroxymethylamino amine, ethanolamine, diethanolamine, aminomethyl propanol, aminomethyl propanediol and the like. The preferred alkaline reagents are ammonium hydroxide, sodium carbonate and ethanolamine. With the reagents listed above, the selected pH will generally be achieved if the composition contains an alkaline agent in an amount from about 0.1% to about 15%, preferably, about 0.5% to about 5%.

The application of the dyeing components is carried out by methods familiar to those in the art, for example, by mixing the hair dyeing preparation with an oxidant shortly before use, or at the time of applying the mixture onto the hair. On the hair, the compositions form a stable formulation with enough consistency and body to remain on the hair without dripping or running during the complete coloring period. The primary intermediate and coupler, i.e. the dye precursors, diffuse rapidly into the hair together with the oxidizing agent, or developer. The dyes form within the hair fiber, and since they are large molecules, remain in the hair

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so that the color change is permanent. The term "permanent" means the dye does not readily wash out of the hair with ordinary shampoos. At the end of coloring application (e.g., approximately 5 to 45 minutes, preferably, approximately 10 to 30 minutes), the composition is washed from the hair with an ordinary water rinse followed by a shampoo. The application temperature is in the range of about 15° C. to 50° C.

The 1-(4-aminophenyl) pyrrolidines, and cosmetically-acceptable derivatives and salts thereof, are soluble in water and have a long shelf life, particularly as constituents of the hair dyeing preparations in accordance with the invention. These primary intermediates, of which 1-(4-aminophenyl) pyrrolidine and 1-(4-amino-3-methylphenyl) pyrrolidine are preferred, should be present in the hair dyeing preparations in an amount of approximately 0.1% to approximately 10%, preferably, approximately 0.1% to approximately 5%. The total quantity of oxidative colorant, consisting of dye component(s) and coupling component(s) will suitably amount to approximately 0.1% to approximately 20%, and preferably, approximately 0.5% to approximately 15% of the composition.

The hair dyeing compounds in accordance with the invention will offer a wide range of varying color tints depending upon the type and composition of the colorant constituents. The color tints are distinguished herein by their particular intense and lasting color. The superior coloring properties of the hair dyeing compositions of the present invention are further evidenced by allowing grayed hair that has not been subjected to prior chemical damage to be covered without problems and with a depth and covering strength that, prior to the discovery of the primary intermediates of the present invention, had only been attained using the conventional PPD.

The compositions of this invention may be separately provided in a kit or packaged form ready for mixing by the user, either professional or consumer, to initiate the dyeing process. The kit provided in accordance with this invention comprises containers for housing the developer and the dye precursors. In the most convenient form, there will be two containers, one containing the primary dye intermediate and coupler, e.g., as a lotion; the other containing the oxidizing agent, also called the developer or developing agent.

The method of the invention comprises applying the mixture to the hair to be colored and allowing it to remain in contact with the hair until the desired hair color has been attained, after which time the composition is removed from the hair as described above.

## EXAMPLES

The examples as set forth herein are meant to exemplify the various aspects of carrying out the invention and are not intended to limit the invention in any way.

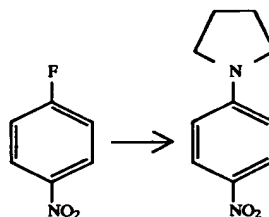
## EXAMPLE 1

1-(4-aminophenyl) pyrrolidine sulfate used in the oxidative hair dye compositions of the present invention was prepared in the following steps:

Step 1. Synthesis of 1-(4-nitrophenyl) pyrrolidine

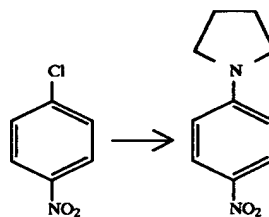
## 12

Route 1: Synthesis from 4-fluoronitrobenzene:



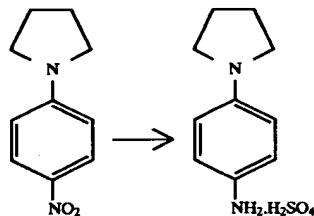
28.2 g (0.2 mole) 4-fluoronitrobenzene were combined with 21 ml (0.25 mole) pyrrolidine, 25.0 g  $\text{Na}_2\text{CO}_3$ , 200 ml  $\text{H}_2\text{O}$ , and the resultant mixture was refluxed with stirring. When TLC showed no evidence of starting material (ca. 3 hours), the mixture was cooled to ambient temperature and then placed in an ice-bath. The mixture was filtered, washed three times with cold  $\text{H}_2\text{O}$  and dried in vacuo at 50° C. The final yield was 38.2 g (99%) of yellow solid.

Route 2: Synthesis from 4-chloronitrobenzene:



15.76 g (0.1 mole) 4-chloronitrobenzene were combined with 18.5 ml (0.22 mole) pyrrolidine, 11.0 g  $\text{Na}_2\text{CO}_3$ , 25 ml 2-propanol and 25 ml  $\text{H}_2\text{O}$ , and the resultant mixture was refluxed with stirring. When TLC showed no evidence of starting material (ca. 14 hours), 75 ml  $\text{H}_2\text{O}$  were added, the mixture was refluxed for 1 hour, cooled to ambient temperature and placed in an ice-bath. The cold mixture was filtered, washed 5 times with cold  $\text{H}_2\text{O}$  and dried in vacuo at 50° C. The final yield was 19.05 g (99%) of yellow solid.

Step 2. Synthesis of 1-(4-aminophenyl) pyrrolidine sulfate:



378.8 g (1.96 moles) 1-(4-nitrophenyl)pyrrolidine, 12.0 g Darco KB carbon, and 10% palladium on carbon (Pd/C) were suspended in 1300 ml ethanol and hydrogenated on a Parr apparatus at 60 psi. When  $\text{H}_2$  uptake ceased and the reaction was complete, the mixture was filtered through filter aid and the resulting "cake" solid was washed 3 times with ethanol (50 ml/wash). The filtrate was stirred in an ice/acetone bath and a cold solution of concentrated  $\text{H}_2\text{SO}_4$  (204 g (2 moles)) in 150 ml ethanol was added dropwise over 1 hour. The resultant precipitate was filtered, washed 4 times with ethanol (100 ml/wash) and dried in vacuo at 50° C. The final yield was 325 g (63%) of white solid. MS (solid probe): m/e 162 (free base).

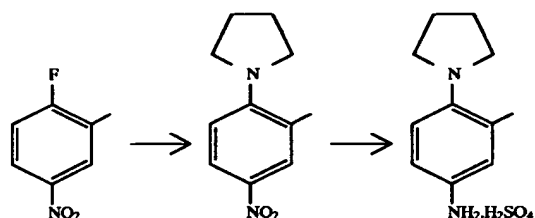
As appreciated by those having skill in the art, additional synthetic routes, such as nitration or nitrosation of

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1-phenylpyrrolidine or its analogs, followed by reduction, may also be used. In addition, other reduction techniques, such as Zn/HCl, may be used, as can other precious metal catalysts, such as Pt/C.

## EXAMPLE 2

Substituted 1-(4-amino-2-methylphenyl) pyrrolidine sulfate, used in the oxidative hair dye compositions of the present invention, was prepared as follows:  
Synthesis of 1-(4-amino-2-methylphenyl)pyrrolidine sulfate:



15.5g (0.1 mole) 2-fluoro-5-nitrotoluene, 25 ml (0.3 mole) pyrrolidine, 11.0 g  $\text{Na}_2\text{CO}_3$  were combined with 50 ml 2-ethoxyethanol and refluxed with stirring. When the TLC showed no evidence of starting material (ca. 2 hours), the mixture was poured onto ice. The precipitate was filtered, washed 5 times with cold  $\text{H}_2\text{O}$ , and dried on filter paper for 2 hours. The resulting solid was mixed with 125 ml 2-propanol, 10% Pd/C, and hydrogenated at 60 psi on a Parr apparatus. The mixture was filtered through filter-aid and stirred with external cooling in an ice/acetone bath. A cold solution of 10.7 g (0.105 mole) concentrated  $\text{H}_2\text{SO}_4$  in 15 ml 2-propanol was added dropwise over 15 minutes. The resultant precipitate was filtered, washed 2 times with 2-propanol and dried in vacuo at  $50^\circ\text{C}$ . The final yield was 24.45 g (89%) of a light grey solid. MS (solid probe): m/e 176 (free base).

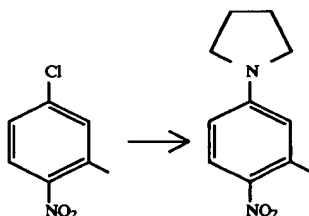
As will be appreciated by those having skill in the art and as described above in Example 1, alternative synthesis procedures may be used. Examples include using 2-chloro-5-nitrotoluene as the starting material, and nitrating or nitrosating 1-(2-methylphenyl)pyrrolidine followed by reduction.

## EXAMPLE 3

1-(4-amino-3-methylphenyl) pyrrolidine sulfate used in the oxidative hair dye compositions of the present invention was prepared as follows:

Synthesis of 1-(4-amino-3-methylphenyl)pyrrolidine sulfate:

Step 1. Synthesis of 1-(4-nitro-3-methylphenyl)pyrrolidine

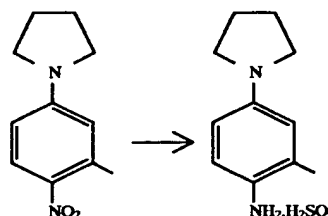


17.16 g (0.1 mole) 5-chloro-2-nitrotoluene were combined with 17 ml (0.2 mole) pyrrolidine, 11.0 g  $\text{Na}_2\text{CO}_3$  and 60 ml 2-ethoxyethanol, and the resultant mixture was refluxed with stirring. When TLC showed no starting mate-

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rial (ca. 9 hours), the mixture was poured onto ice. The resultant precipitate was filtered, washed 5 times with cold  $\text{H}_2\text{O}$  and dried in vacuo at  $50^\circ\text{C}$ . The final yield was 20.25 g (98%) of orange solid.

Step 2. Synthesis of 1-(4-amino-3-methylphenyl) pyrrolidine sulfate



20.25 g (0.098 mole) 1-(4-nitro-3-methylphenyl) pyrrolidine were combined with 2 g Darco KB carbon, 200 ml 2-propanol and 5% Pd/C. The mixture was hydrogenated at 60 psi on a Parr apparatus. When reduction was complete, the mixture was filtered through filter aid and stirred with external cooling in an ice/acetone bath. A cold solution of 10.72 g (0.105 mole) concentrated  $\text{H}_2\text{SO}_4$  in 20 ml 2-propanol was added dropwise and stirred for 1 hour. The mixture was filtered, washed 2 times with 2-propanol, and dried in vacuo at  $50^\circ\text{C}$ . The final yield was 22.3 g (83%) of off-white solid. MS (solid probe): m/e 176 (free base).

As mentioned hereinabove, alternative syntheses and reduction techniques may also be used. For example, 5-fluoro-2-nitrotoluene can be used as the starting material and 1-(3-methylphenyl)pyrrolidine can be nitrated or nitrosated and reduced.

## EXAMPLES 4 TO 13

Hair dyeing compositions in accordance with the invention (Examples 4-13) were prepared as presented in Table 1. The compositions were in the form of lotions. Illustrative lotion compositions of this invention and the color results following the application of the compositions to gray hair are shown in Table 1.

TABLE 1

Components	EXAMPLES:				
	4	5	6	7	8
	Amounts of Components				
1-(4-aminophenyl) pyrrolidine sulfate	1.0	3.5	0.3	0.1	0.1
p-phenylenediamine	—	—	—	—	0.1
N,N-bis(2-hydroxyethyl)-PPD sulfate	—	0.5	—	—	—
4-aminophenol	—	—	0.1	—	0.2
3-methyl-4-aminophenol	—	—	—	0.2	—
m-aminophenol	0.5	1.5	—	—	0.1
resorcinol	0.5	1.5	0.4	0.2	0.5
1-naphthol	0.1	—	—	—	0.1
2-methyl-1-naphthol	—	—	0.1	0.1	—
4-amino-2-hydroxytoluene	—	—	—	0.4	0.3
p-phenylenediamine	—	0.2	—	—	—
isopropanol	10	10	10	10	10
propylene glycol	15	15	15	15	15
oleic acid	14	14	14	14	14
monoxynol-2	9	9	9	9	9
cocamide DEA	1	1	1	1	1
ammonium hydroxide	10	10	10	10	10
sodium sulfite	0.1	0.1	0.1	0.1	0.1

TABLE 1-continued

Components	EXAMPLES:				
	4	5	6	7	8
	Amounts of Components				
	wt %	wt %	wt %	wt %	wt %
water	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100
Color Results on Gray Hair	Dark Brown	Blue Black	Light Brown	Auburn	Reddish Brown

## EXAMPLES 9 TO 13

Hair dyeing lotion compositions in accordance with the present invention (Examples 9 to 13) were prepared as presented in Table 2. Illustrative lotion compositions of this invention and the color results following the application of the composition to gray hair are presented in Table 2:

TABLE 2

Components	EXAMPLES:				
	9	10	11	12	13
	Amounts of Components				
	wt %	wt %	wt %	wt %	wt %
1-(4-aminophenyl) pyrrolidine sulfate	1.0	3.5	0.3	0.1	0.1
p-phenylenediamine	—	—	—	—	0.1
N,N-bis(2-hydroxyethyl)-PPD sulfate	—	0.5	—	—	—
4-aminophenol	—	—	0.1	—	0.2
3-methyl-4-aminophenol	—	—	—	0.2	—
m-aminophenol	0.5	1.5	—	—	0.1
resorcinol	0.5	1.5	0.4	0.2	0.5
1-naphthol	0.1	—	—	—	0.1
2-methyl-1-naphthol	—	—	0.1	0.1	—
4-amino-2-hydroxytoluene	—	—	—	0.4	0.3
m-phenylenediamine	—	0.2	—	—	—
cocamidopropyl betaine	10	10	10	10	10
monoethanol amine	2	2	2	2	2
citric acid	1	1	1	1	1
ammonium hydroxide	10	10	10	10	10
sodium sulfite	0.1	0.1	0.1	0.1	0.1
water	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100
Color Results on Gray Hair	Dark Brown	Blue Black	Light Brown	Auburn	Reddish Brown

## EXAMPLES 14 TO 18

Hair dyeing gel compositions in accordance with the present invention (Examples 14 to 18) were prepared as presented in Table 3. Illustrative gel compositions of this invention and the color results following the application of the composition to gray hair are presented in Table 3:

TABLE 3

Components	EXAMPLES:				
	14	15	16	17	18
	Amounts of Components				
	wt %	wt %	wt %	wt %	wt %
1-(4-aminophenyl) pyrrolidine sulfate	1.0	3.5	0.3	0.1	0.1

TABLE 3-continued

Components	EXAMPLES:				
	14	15	16	17	18
	Amounts of Components				
	wt %	wt %	wt %	wt %	wt %
p-phenylenediamine	—	—	—	—	0.1
N,N-bis(2-hydroxyethyl)-PPD sulfate	—	0.5	—	—	—
4-aminophenol	—	—	0.1	—	0.2
3-methyl-4-aminophenol	—	—	—	0.2	—
m-aminophenol	0.5	1.5	—	—	0.1
resorcinol	0.5	1.5	0.4	0.2	0.5
1-naphthol	0.1	—	—	—	0.1
2-methyl-1-naphthol	—	—	0.1	0.1	—
4-amino-2-hydroxytoluene	—	—	—	0.4	0.3
m-phenylenediamine	—	0.2	—	—	—
cocamidopropyl betaine	10	10	10	10	10
monoethanol amine	2	2	2	2	2
oleic acid	5	5	5	5	5
decyl polyglucoside	5	5	5	5	5
ammonium hydroxide	10	10	10	10	10
sodium sulfite	0.1	0.1	0.1	0.1	0.1
water	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100
Color Results on Gray Hair	Dark Brown	Blue Black	Light Brown	Auburn	Reddish Brown

## EXAMPLE 19

Table 4 presents the results of the hair dyeing performance of the 1-(4-aminophenyl) pyrrolidine primary intermediate (Compound 6 in Table 4) in compositions of the invention compared with that of PPD (Compound 1 in Table 4) and various analogs of PPD, using 3-aminophenol as coupling agent (Table 4). For these evaluations, equimolar amounts of the primary dye intermediate (0.2M) and the coupling agent (0.2 M) were used (for examples, see Tables 1-3). The primary intermediate and coupling agent were mixed with 20 vol. hydrogen peroxide immediately before use, and the mixture was subsequently applied to blended gray hair swatches. The treatment period was for 30 minutes at room temperature; thereafter, the dyed hair was rinsed with water and dried.

In Table 4, "L", "a", and "b" represent the standard Hunter Tristimulus values which measure the depth and tonality of the color. In the Hunter method, the parameters a and b may be positive or negative and define the chromatic condition of the hair. Thus, the more positive the a value, the greater the redness of the hair, while negative a values indicate greenness. Similarly, positive b values indicate yellowness, while negative b values indicate blueness. The L parameter is a measure of color intensity and has a value of 0 for absolute black to 100 for absolute white.

TABLE 4

Hair Dyeing Performance of PPD Versus Various 1-(4-aminophenyl) pyrrolidine Compounds of the Present Invention (i.e., PPD Analogs) With 3-Aminophenol As Coupling Compound						
Dye Compound No.	Chemical Name of Dye Compound Used As Primary Intermediate	L a b			$\Delta H^*$	$\Delta E^*$
		L	a	b		
1	PPD	21.0	0.4	-0.5		
2	2-methyl PPD	22.0	1.0	0.1	0.85	1.31

TABLE 4-continued

Hair Dyeing Performance of PPD Versus Various 1-(4-aminophenyl) pyrrolidine Compounds of the Present Invention (i.e., PPD Analogs) With 3-Aminophenol As Coupling Compound

Dye Compound No.	Chemical Name of Dye Compound Used As Primary Intermediate	L	a	b	$\Delta H^*$	$\Delta E^*$
3	2-(2-hydroxyethyl) PPD	26	1.6	3.0	3.7	6.22
4	2-chloro PPD	25.5	2.9	-1.0	2.55	5.17
5	N,N-bis(2-hydroxyethyl) PPD	23.5	0.4	-3.8	3.3	3.09
6	1-(4-aminophenyl) pyrrolidine	21.2	0.5	-1.0	0.51	0.55
7	1-(4-aminophenyl) piperidine	27.1	1.8	2.2	3.04	6.82
8	4-(4-aminophenyl) morpholine	27.1	3.8	2.0	4.22	7.42
9	N,N-dimethyl PPD	25.9	0.1	1.6	2.12	5.34

\*versus PPD

From the data presented in Table 4, it can be observed that compound 6 (1-(4-aminophenyl) pyrrolidine) of the present invention is the closest match to PPD (compound 1) in color tone and intensity when coupled with 3-aminophenol. The difference in color tone is measured by  $\Delta H = [(\Delta a)^2 + (\Delta b)^2]^{1/2}$  and total color difference, as determined by  $\Delta E = [(\Delta a)^2 + (\Delta b)^2 + (\Delta L)^2]^{1/2}$ . Both the  $\Delta H$  and the  $\Delta E$  values for any compound versus PPD are the smallest for compound 6 (i.e., 1-(4-aminophenyl) pyrrolidine) of the invention. Compound 2, (2-methyl PPD), the ring-substituted intermediate conventionally used in commercial hair dye products, is the next closest. None of the other compounds are as close to PPD in either intensity or tonality, including compound 3 (2-(2-hydroxyethyl) PPD). These results demonstrate that compound 6 of the present invention can be employed as a replacement, in whole or in part, for PPD with little or no difference in tone or intensity of color.

The formation of an intense neutral color from the 1-(4-aminophenyl) pyrrolidine compound combined with 3-aminophenol, as coupler, was completely unexpected prior to the present invention, since this color is far different from that formed by close chemical analogs of 1-(4-aminophenyl) pyrrolidine, i.e., compounds 5, 7, 8 and 9, with 3-aminophenol. Indeed, although the aforementioned compounds are N,N-disubstituted or N-cyclic compounds, similar to 1-(4-aminophenyl) pyrrolidine, only 1-(4-aminophenyl) pyrrolidine matches virtually identically with the N-unsubstituted PPD in color formation. These findings were evidenced both for the difference in color tone (i.e.,  $\Delta H$  versus PPD) and for the variation in total color ( $\Delta E$  versus PPD).

#### EXAMPLE 20

In this example, the hair dyeing performance of unsubstituted 1-(4-aminophenyl) pyrrolidine (compound 6), 1-(4-amino-2-methylphenyl) pyrrolidine (compound 10) and 1-(4-amino-3-methylphenyl) pyrrolidine (compound 11), as primary intermediates in the compositions of the invention, was evaluated in combination with the different coupling agents presented in Table 5.

For these analyses, blended and bleached hair swatches were dyed for 30 minutes with compositions comprising 0.2M primary intermediate and 0.2M coupler in a cosmetically acceptable hair dye base (for examples, see Tables 1-3) plus 20 vol.  $H_2O_2$ , followed by a water rinse and air drying.

TABLE 5

Hair Color Products Obtained From 1-(4-Aminophenyl) Pyrrolidines of the Present Invention Reacted With Various Couplers

Compound	Coupler	Color	
		Blended Grey	Bleached
6	3-aminophenol	Bluish black	Neutral black
6	resorcinol	Dark brown	Neutral black
6	2-methylresorcinol	Dark reddish	Neutral black
6	2-hydroxy-4-amino-toluene	Violet black	Neutral black
6	1-naphthol	Blue	Purplish black
6	2-methyl-1-naphthol	Violet blue	Dark violet blue
10	3-aminophenol	Medium brown	Dark brown
10	2-hydroxy-4-amino-toluene	Violet	Dark violet
10	1-naphthol	Violet blue	Deep blue
11	3-aminophenol	Bluish black	Neutral black
11	2-hydroxy-4-amino-toluene	Dark blue	Bluish black
11	1-naphthol	Bright blue	Violet
11	resorcinol	Reddish brown	Dark brown
11	2-methylresorcinol	Medium brown	Dark warm brown
11	2-methyl-1-naphthol	Navy blue	Violet blue
6	2-(2,4-diaminophenoxy) ethanol	Dark blue	Neutral black
11	2-(2,4-diaminophenoxy) ethanol	Blue	Bluish black

In Table 5, compound 6 is unsubstituted 1-(4-aminophenyl) pyrrolidine, compound 10 is 1-(4-amino-2-methylphenyl) pyrrolidine and compound 11 is 1-(4-amino-3-methylphenyl) pyrrolidine. The structures of compounds 10 and 11 are shown as Formulae II and III, respectively, in the Detailed Description of the Invention hereinabove.

The results from these evaluations demonstrate that the color produced using the unsubstituted and substituted 1-(4-aminophenyl) pyrrolidine compounds of the invention, namely 1-(4-aminophenyl) pyrrolidine, 1-(4-amino-2-methylphenyl) pyrrolidine and 1-(4-amino-3-methylphenyl) pyrrolidine, as primary intermediates in hair dye compositions, was intense and vivid. In addition, different coloration and nuances could be achieved using the compounds of the invention as primary intermediates in combination with various conventionally-used couplers. The newly-discovered compound 11 afforded surprising performance in coloring both gray and bleached hair compared with the coloration produced by compound 10 using the same coupling agents. Further, the results presented in Table 5 exemplify novel hair colors which are the reaction products of compounds of the present invention, e.g., compounds 6, 10 and 11, with particularly suitable couplers.

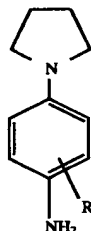
The contents of all patents, patent applications, published articles, books, reference manuals and abstracts cited herein are hereby incorporated by reference in their entirety to more fully describe the state of the art to which the invention pertains.

As various changes can be made in the above-described subject matter without departing from the scope and spirit of the invention, it is intended that all subject matter contained in the above description, shown in the accompanying drawings, or defined in the appended claims be interpreted as descriptive and illustrative, and not in a limiting sense. Many modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

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What is claimed is:

1. In a composition for the oxidative coloring of hair, said composition containing a primary dye intermediate, a coupling compound, a cosmetically acceptable oxidizing agent selected from the group consisting of hydrogen peroxide, urea peroxide, melamine peroxide, perborates, and percarbonates, and a cosmetically acceptable vehicle, wherein said primary dye intermediate and said coupling compound form an oxidative hair dye in the presence of said cosmetically acceptable oxidizing agent, the improvement which comprises said primary dye intermediate is a 1-(4-aminophenyl) pyrrolidine, or a cosmetically acceptable salt thereof, having formula I:



wherein R is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>6</sub> alkyl and C<sub>1</sub>-C<sub>5</sub> mono or polyhydroxyalkyl.

2. The composition according to claim 1, wherein R is hydrogen or methyl.

3. The composition according to claim 2, wherein R is hydrogen.

4. The composition according to claim 2, wherein R is methyl.

5. The composition according to claim 4, wherein said methyl is at the 2-position of the phenyl ring of said 1-(4-aminophenyl) pyrrolidine or cosmetically acceptable salt thereof.

6. The composition according to claim 4, wherein said methyl is at the 3-position of the phenyl ring of said 1-(4-aminophenyl) pyrrolidine or cosmetically acceptable salt thereof.

7. The composition according to claim 1, wherein R is hydrogen, C<sub>1</sub>-C<sub>2</sub> alkyl, or C<sub>1</sub>-C<sub>3</sub> monohydroxyalkyl.

8. The composition according to claim 1, wherein said 1-(4-aminophenyl) pyrrolidine is present in an amount of about 0.01% to about 10%, by weight, based on the total weight of the composition.

9. The composition according to claim 1, wherein said coupling compound is present in an amount of about 0.1% to about 10%, by weight, based on the total weight of the composition.

10. The composition according to claim 8, wherein said 1-(4-aminophenyl) pyrrolidine primary intermediate is present at about 0.1% to about 5%, by weight, based on the total weight of the composition.

11. The composition according to claim 9, wherein the coupling compound is present in an amount of about 0.1% to about 5%, by weight, based on the total weight of the composition.

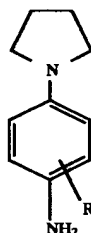
12. The composition according to claim 1, further including one or more additional dye components selected from the group consisting of p-phenylenediamine and cosmetically acceptable derivatives thereof; p-aminophenols and cosmetically acceptable derivatives thereof; ortho developers and cosmetically acceptable derivatives thereof; phenols and cosmetically acceptable derivatives thereof; resorcinols and cosmetically acceptable derivatives thereof; m-phenylenediamines and cosmetically acceptable derivatives thereof; m-aminophenols and cosmetically acceptable derivatives thereof; and heterocyclic derivatives.

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13. The composition according to claim 1, wherein said coupling compound is selected from the group consisting of 3-aminophenol, resorcinol, 2-methylresorcinol, 2-hydroxy-4-aminotoluene, 1-naphthol, 2-methyl-1-naphthol and 2-(2,4-diaminophenoxy)ethanol.

14. The composition according to claim 1, wherein said oxidizing agent is hydrogen peroxide.

15. An oxidative hair dye product produced by reacting, in a cosmetically acceptable vehicle and in the presence of a cosmetically acceptable oxidizing agent selected from the group consisting of hydrogen peroxide, urea peroxide, melamine peroxide, perborates, and percarbonates, a coupling compound and a 1-(4-aminophenyl) pyrrolidine, or a cosmetically acceptable salt thereof, having the formula I:



wherein R is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>6</sub> alkyl and C<sub>1</sub>-C<sub>5</sub> mono or polyhydroxyalkyl.

16. The hair dye product according to claim 15, wherein R is hydrogen or methyl.

17. The hair dye product according to claim 16, wherein R is hydrogen.

18. The hair dye product according to claim 16, wherein R is methyl.

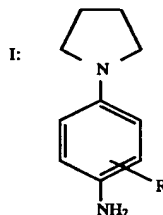
19. The hair dye product according to claim 18, wherein said methyl is at the 2-position of the phenyl ring of said 1-(4-aminophenyl) pyrrolidine or cosmetically acceptable salt thereof.

20. The hair dye product according to claim 18, wherein said methyl is at the 3-position of the phenyl ring of said 1-(4-aminophenyl) pyrrolidine or cosmetically acceptable salt thereof.

21. The hair dye product according to claim 15, wherein R is hydrogen, C<sub>1</sub>-C<sub>2</sub> alkyl, or C<sub>1</sub>-C<sub>3</sub> monohydroxyalkyl.

22. The hair dye product according to claim 15, wherein said coupling compound is selected from the group consisting of 3-aminophenol, 2-hydroxy-4-aminotoluene, resorcinol, 2-methylresorcinol, 1-naphthol, 2-methyl-1-naphthol and 2-(2,4-diaminophenoxy) ethanol.

23. A hair dye product formed by reacting equimolar amounts of (i) a 1-(4-aminophenyl) pyrrolidine, or a cosmetically acceptable salt thereof, having the formula I:



wherein R is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>6</sub> alkyl and C<sub>1</sub>-C<sub>5</sub> mono or polyhydroxyalkyl, (ii) a coupling agent, and (iii) a cosmetically acceptable oxidizing agent selected from the group consisting of hydrogen peroxide, urea peroxide, melamine peroxide, perborates, and percarbonates, in a cosmetically acceptable vehicle.



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24. The hair dye product according to claim 23, wherein R is hydrogen or methyl.

25. The hair dye product according to claim 24, wherein said methyl is at the 2-position of the phenyl ring of said 1-(4-aminophenyl) pyrrolidine or cosmetically acceptable salt thereof.

26. The hair dye product according to claim 24, wherein said methyl is at the 3-position of the phenyl ring of said 1-(4-aminophenyl) pyrrolidine or cosmetically acceptable salt thereof.

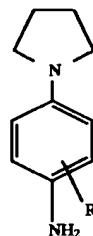
27. The hair dye product according to claim 23, wherein R is hydrogen, C<sub>1</sub>-C<sub>2</sub> alkyl, or C<sub>1</sub>-C<sub>3</sub> monohydroxyalkyl.

28. The hair dye product according to claim 23, wherein said coupling agent is selected from the group consisting of 3-aminophenol, 2-hydroxy-4-aminotoluene, resorcinol, 2-methylresorcinol, 1-naphthol, 2-methyl-1-naphthol and 2-(2,4-diaminophenoxy) ethanol.

29. A method for the oxidative coloring of a keratin fiber comprising contacting the fiber with a fiber coloring effective amount of a composition containing a 1-(4-

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aminophenyl) pyrrolidine, or a cosmetically acceptable salt thereof, having Formula I:



I:

wherein R is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>6</sub> alkyl and C<sub>1</sub>-C<sub>3</sub> mono or polyhydroxyalkyl, a coupling compound and a cosmetically acceptable oxidizing agent, in a cosmetically acceptable vehicle; and maintaining contact with the fiber until the fiber is colored.

30. The method according to claim 29 wherein the fiber is human hair.

\* \* \* \* \*



US005961666A

**United States Patent** [19]**Lim et al.**[11] **Patent Number:** **5,961,666**[45] **Date of Patent:** **Oct. 5, 1999**

[54] **HAIR DYE COMPOSITIONS CONTAINING 3-SUBSTITUTED-4-AMINOPHENOLS AND 2-SUBSTITUTED-1-NAPHTHOLS**

[76] **Inventors:** **Mu-III Lim**, 31 Mayflower Dr., Trumbull, Conn. 06611; **Yuh-Guo Pan**, 119 Woodridge Dr., Stamford, Conn. 06905; **James S. Anderson**, 1 Summit La., Bethel, Conn. 06801

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[51] **Int. Cl.<sup>6</sup>** ..... **A61K 7/13**

[52] **U.S. Cl.** ..... **8/408; 8/421; 8/424**

[58] **Field of Search** ..... **8/406, 408, 421, 8/424**

[56] **References Cited**

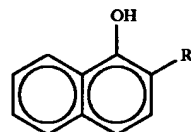
**U.S. PATENT DOCUMENTS**

3,210,252	10/1965	Blanke et al.	8/408
4,169,703	10/1979	Fahouri	8/421
4,883,656	11/1989	Konrad et al.	8/408
5,344,463	9/1994	Chan et al.	8/408
5,409,503	4/1995	Clausen et al.	8/408
5,500,021	3/1996	Cotteret et al.	8/408
5,514,188	5/1996	Cotteret et al.	8/408
5,567,421	10/1996	Cotteret et al.	8/408
5,580,357	12/1996	Cotteret et al.	8/421

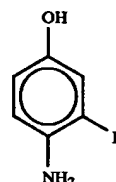
*Primary Examiner*—Caroline D. Liott  
*Attorney, Agent, or Firm*—Morton S. Simon

[57] **ABSTRACT**

A 2-Substituted-1-naphthol of the formula:



wherein R<sub>1</sub> is C<sub>1</sub>–C<sub>6</sub> alkyl or monohydroxy C<sub>1</sub>–C<sub>6</sub> alkyl couples with a primary intermediate of the formula:



wherein R is C<sub>1</sub>–C<sub>6</sub> alkyl or monohydroxy C<sub>1</sub>–C<sub>6</sub> alkyl to produce an oxidative dye.

**11 Claims, No Drawings**

# HAIR DYE COMPOSITIONS CONTAINING 3-SUBSTITUTED-4-AMINOPHENOLS AND 2-SUBSTITUTED-1-NAPHTHOLS

## FIELD OF INVENTION

The present invention relates to oxidative keratinous dyeing compositions based on 4-aminophenols and 1-naphthols.

## BACKGROUND OF THE INVENTION

U.S. Pat. No. 3,210,252 discloses oxidation dyeing compositions containing 5-amino-2-methylphenol (1-methyl-2-hydroxy-4-aminobenzene) in combination with p-phenylene-diamine (PPD) or PPD derivatives or p-aminophenol (PAP) or PAP derivatives. In the presence of an oxidizing agent these compositions dye hair brilliant color shades such as gold red, mahogany and Bordeaux. PAP derivatives include compounds such as 3-methyl-4-aminophenol and 2-methyl-4-aminophenol.

U.S. Pat. No. 4,883,656 (the '656 patent) covers compositions for the oxidative dyeing of hair comprising a specific composition of 3-methyl-4-aminophenol, 2-methyl-5-aminophenol and PPD or p-toluenediamine (PTD) or mixtures thereof. Natural red, free of yellow and blue hues, was obtained.

The '656 patent teaches that 3-methyl-4-aminophenol is not good in conventional terms. It is disclosed that "although the developer substance 3-methyl-4-aminophenol is frequently mentioned in publications on hair dyeing, it has achieved very little importance, if any, in practice. Thus, 3-methyl-4-aminophenol with 2-methyl-5-aminophenol as coupler only provides a brick red which is weak in color."

U.S. Pat. No. 4,997,451 ('451 patent) relates to oxidative hair dyeing compositions based on 4-aminophenol derivatives and new 4-aminophenol derivatives.

The '451 patent covers dyeing compositions containing 2-(alkoxymethyl)-4-aminophenol as the developer substance and teaches that "the 4-amino-3-methylphenol, which is a structurally similar compound, results in a considerably reduced color depth than the 4-aminophenol derivatives of the present invention."

U.S. Pat. No. 5,344,463 (the '463 patent) relates to hair dye compositions and methods utilizing 2-substituted-1-naphthol couplers.

The '463 patent deals with dye composition containing 2-substituted-1-naphthol in which the composition imparts a long-lasting red color to hair. The compositions of this patent are taught to be substantially more acid-resistant than dyestuffs prepared through use of the 1-naphthol coupler.

3-Methyl-4-aminophenol is mentioned as one of the primary intermediates in the '463 patent. However, there is no teaching that the combination of 3-methyl-4-aminophenol and 2-methyl-1-naphthol delivers color to hair which is unusually and unexpectedly shampoo- and light-fast.

U.S. Pat. No. 5,500,021 ('021 patent) relates to an oxidation dye composition for keratinous fibers comprising a para-aminophenol, a meta-aminophenol and a meta-phenylenediamine, and dyeing process using such a composition.

The combination of 3-methyl-4-aminophenol, 2-methyl-5-aminophenol and PPD or PTD produces coloration with warm and coppery shades which have good resistance to light, to washing, to bad weather, and to perspiration. The '021 patent teaches that the composition gives resistance to perspiration which is particularly noteworthy and superior to that of the state of the art.

U.S. Pat. No. 5,514,188 discloses oxidation dye compositions for keratinous fibers comprising a 4-aminophenol, 2-methyl-5-aminophenol and p-phenylenediamine and/or a bis(phenylalkylene)diamine.

Combinations of 3-Methyl-4-aminophenol or 2-methyl-4-aminophenol, or 2-hydroxymethyl-4-aminophenol with 2-methyl-5-aminophenol and PPD derivatives produce colorations with red or coppery shades which are resistant to light, to washing, to bad weather, and to perspiration.

U.S. Pat. No. 4,883,656 characterizes 3-methyl-4-aminophenol as achieving very little importance in practice and that compositions containing this intermediate provide a brick red which is weak in color.

U.S. Pat. No. 4,997,451 also teaches that 3-methyl-4-aminophenol produces a considerably reduced color depth than 4-aminophenol.

U.S. Pat. Nos. 4,883,656 and 4,997,451 teach that 3-methyl-4-aminophenol does not produce good color useful enough to use as a hair dye. U.S. Pat. No. 5,500,021 and U.S. Pat. No. 5,514,188 also teach that 3-methyl-4-aminophenol is only useful when it is used in combination with 2-methyl-5-aminophenol and m-diaminobenzene or p-diaminobenzene.

## SUMMARY OF THE INVENTION

The present invention relates to a dyeing composition for keratinous fibers, and in particular, for human keratinous fibers, said composition comprising 3-alkyl-4-aminophenol and 2-alkyl-1-naphthol and to a dyeing process using this combination.

## DETAILED DESCRIPTION OF THE INVENTION

It has surprisingly been found that the use of the combination of a 3-alkyl-4-aminophenol and 2-alkyl-1-naphthol has several advantages.

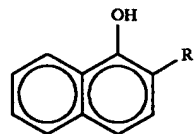
U.S. Pat. Nos. 4,883,656 and 4,997,451 teach that when used with only one coupler 3-methyl-4-aminophenol is expected to deliver weaker coloration to hair than 4-aminophenol. To the present inventors' surprise, the color depth obtained from 3-methyl-4-aminophenol (3-Mepap) and 2-methyl-1-naphthol is as strong as 4-aminophenol on gray hair and significantly stronger on bleached hair.

Wash fastness of the dye produced by coupling 3-methyl-4-aminophenol with 2-methyl-1-naphthol, is far better than the wash fastness of the dye produced by coupling 4-aminophenol with 2-methyl-1-naphthol. The  $\Delta E$  value of the dye resulting from the former intermediate is smaller than the value of the dye resulting from latter intermediate (see Table 3, below).  $\Delta E$  indicates the magnitude of the color difference. The smaller the  $\Delta E$  value, the better the fastness.  $\Delta E$  is defined as

$$\sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

wherein L is a measure of color depth (i.e. darkness) a and b indicate color directions: +a is the red direction; -a is the green direction; +b is the yellow direction; and -b is the blue direction.

The present invention relates to the use of 2-substituted-1-naphthols of the general formula I:

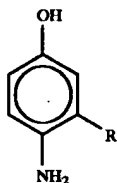


wherein R<sub>1</sub> is C<sub>1</sub>-C<sub>6</sub> alkyl or monohydroxy C<sub>1</sub>-C<sub>6</sub> alkyl. Preferred couplers in this aspect of the invention are:

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2-methyl-1-naphthol, 2-hydroxymethyl-1-naphthol;  
2-ethyl-1-naphthol, 2-(2-hydroxyethyl)-1-naphthol;  
2-propyl-1-naphthol, 2-(3-hydroxypropyl)-1-naphthol.  
4-aminophenols are useful in the present invention to conform to the general formula II.

(II)



wherein R is C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>1</sub>-C<sub>6</sub> monohydroxyalkyl.

Preferred 4-aminophenols include:

3-methyl-4-aminophenol, 3-hydroxymethyl-4-aminophenol  
3-ethyl-4-aminophenol, 3-(2-hydroxyethyl)-4-aminophenol  
3-propyl-4-aminophenol, 3-(3-hydroxypropyl)-4-aminophenol.

The 2-substituted naphthol of formula I and the p-aminophenol of formula II are present in the compositions in amounts such that when reacted in the presence of an oxidizing agent a tinctorially effective amount of an oxidation hair dye is produced.

The hair dye preparations of the present invention may be formulated into cosmetic preparations such as solutions, creams, lotions, gels or emulsions. Also, in accordance with the invention, the compositions may in addition to the mixture of the coloring components (i.e., dye intermediate of formula II and coupling agent of formula I) include other coloring components (e.g. couplers and/or intermediates), as well as components commonly associated with the formulation of solutions, creams, lotions, gels or emulsions, and the like. For example, components such as wetting agents or emulsifying agents from the categories of anionic or non-ionic surfactants, such as sulfates of fatty alcohols, alkanolamides of fatty alcohols, alkyl sulfonates, alkylbenzene sulfonates, oxyethylated fatty alcohols, oxyethylated nonylphenols. Additionally, thickeners, such as fatty alcohols, starch, cellulose derivatives, paraffin oil and fatty acids, as well as hair-care substances, such as lanolin derivatives, cholesterol and pantothenic acid, may be formulated into the compositions of the invention.

When formulated as a lotion, the compositions of the invention may contain organic solvents to assist in dissolving the dye precursors. Accordingly, the organic solvent content of the lotion may be from 0% to about 20%, preferably about 1% to 15%. Typically useful solvents include alcohols containing up to three carbon atoms, such as ethanol and isopropanol, polyhydroxy alcohols, such as propylene or hexylene glycol, and lower alkyl ethers thereof, such as ethoxy ethers.

It should be noted that unless otherwise indicated to the contrary all percents specified herein are percent by weight and are based upon the total weight of the composition.

In addition, the hair dyeing compositions in accordance with the present invention may optionally contain conventionally-used adjuvants and cosmetic additives, or mixtures thereof, to achieve the final formulations. Examples of such additives include, but are not limited to, anti-oxidants, e.g. ascorbic acid, erythorbic acid, or sodium

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sulfite, to inhibit premature oxidizing; oxidizing agents, fragrances and/or perfume oils; chelating agents; emulsifiers; coloring agents; thickeners; organic solvents; opacifying agents; dispersing agents; sequestering agents; hair-care substances; humectants; anti-microbials; acidifying agents and others. The list of optional ingredients is not intended as limiting. Other suitable adjuvants for inclusion in the hair dye compositions of the invention are disclosed, for example, in Zviak, *The Science of Hair Care* (1986) and in Balsam and Sagarin, *Cosmetics: Science and Technology*, Vol. 2, Second Edition, (1972).

Thickeners that may be used in the compositions of the present invention include a variety of fatty acid soaps and associative polymeric thickeners. The fatty acid soaps are alkali metal salts or alkanolamine salts of fatty acids with C<sub>10</sub>-C<sub>16</sub> alkyl side chains. The preferred fatty acids include oleic acid, myristic acid, stearic acid and lauric acid, which are generally present in the compositions of the invention at about 0.5% to 20%, preferably about 1% to 10%. Associative thickeners are polymers that can thicken solutions at low concentrations. Among the associative thickeners that are useful in the compositions of the present invention are acrylates copolymer (sold by Rohm and Haas under the trade name Aculyn-33), cetareth-20 acrylates/steareth-20 methacrylate copolymer (sold by Rohm and Haas under the trade name Aculyn-22), acrylates/steareth-20 itaconate copolymer and acrylates/ceteth-20 itaconate copolymer. Another class of associative thickeners useful in the compositions of the present invention include the copolymers of polyurethane and polyethylene glycol or polyetherurethanes. One such illustrative material is sold by Rohm and Haas under the trade name Aculyn-44. The associative polymeric thickeners are generally present in the compositions of the invention at about 0.1% to 10%, preferably about 0.5% to 5%.

The oxidative coupling, i.e., the development of the dye, can, in principle, be performed with atmospheric oxygen to produce the final color product on the hair. However, chemical oxidizing agents are suitably and preferably used. A preferred oxidizing agent for use as a developer or developing agent with the primary intermediates and the couplers of the invention is hydrogen peroxide, although other peroxides may be employed. These include, for example, urea peroxide, melamine peroxide, perborates and percarbonates such as sodium perborate or percarbonate. The concentration of peroxide in the developer may be from about 0.5% to about 40%, preferably about 0.5% to 30%. If the preferred hydrogen peroxide is employed, the concentration will be from about 0.5% to about 12%, preferably about 3% to 9%.

The compositions of the invention may include a typical anionic, cationic, nonionic or amphoteric surfactant.

The anionic surfactants include the variety of alkyl sulfates, alkylether sulfates, alkyl sulfonates, alkyl sulfosuccinates and N-acyl sarcosinates. The commonly-used anionic surfactants are sodium and ammonium lauryl sulfates, sodium and ammonium laureth sulfate and alpha olefin sulfonates. Anionic surfactants are generally present in the compositions of the present invention at about 0.1% to 15%, preferably about 0.5% to 10%.

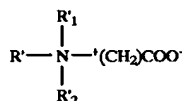
The nonionic surfactants that can be used in the present invention include the wide variety of ethoxylated alcohols, nonoxynols, alkanolamides, alkyl stearates, alkyl palmitates and alkylpolyglucosides. Examples of the commonly-used nonionic surfactants are cetyl alcohol, stearyl alcohol, oleyl alcohol, the various types of ethoxylated alkylphenols; lauramide DEA; lauramide MEA; isopropyl palmitate, isopropyl stearate and decylpolyglucoside. Nonionic surfactants

are generally present in the compositions of the present invention at about 0.1% to 15%, preferably about 0.5% to 10%.

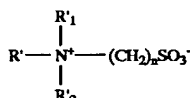
The compositions in accordance with the present invention may also contain one or more quaternary ammonium compounds that provide hair conditioning effects. The quaternary ammonium compounds can be monomeric or polymeric quaternary ammonium compounds. Nonlimiting examples of such compounds include cetyltrimonium chloride, stearyl trimonium chloride, benzalkonium chloride, behentrimonium chloride and a variety of polyquaterniums. The quaternary ammonium compounds are generally present in the compositions of the present invention at about 0.1% to 10%, preferably 0.5% to 5%, of the final composition.

Amphoteric surfactants may be employed in the compositions of the present invention. Amphoteric surfactants are surface active chemicals that possess a positive and a negative charge in the same molecule and behave as a cation, an anion, or both, depending upon the pH of the medium and the nature of the amphoteric molecule. In general, the positive charge is located on a nitrogen, while the negative charge is carried by a carboxyl or sulfonate group. There are a large number of amphoteric surfactants that are suitable for use in the present invention, including, for example, the well-known betaines, sultaines, glycines and propionates that may generally be represented by the following structural formulae:

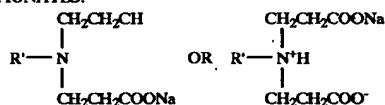
1. BETAINES:



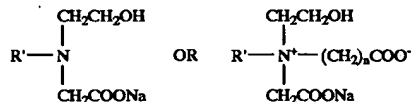
2. SULTAINES:



3. PROPIONATES:



4. GLYCINATES:



In these formulae, R' is an alkyl or alkylamide group containing from 10 to 20 carbon atoms. R'<sub>1</sub> and R'<sub>2</sub> are alkyl or hydroxyalkyl groups, which may be the same or different, and contain up to five carbon atoms. n is a positive integer from one to five.

The selection of the amphoteric surfactant or mixture of surfactants for use in the present compositions and methods is not critical. The surfactant may be selected from among those suggested above, or from any of a number of other known amphoteric surfactants. The amount of amphoteric surfactant in the compositions of the present invention is normally from about 0.5% to about 15%, preferably about 2% to 10%.

Depending on the final formulated preparation, the compositions in accordance with invention may be weakly acidic, neutral or alkaline. In particular the pH of the

prepared compositions can range from about 5 to 11. Preferred is a pH range of about 8 to 10. Any of a wide variety of alkaline reagents can be used to adjust the pH of the hair coloring compositions. Such alkaline reagents include ammonium hydroxide, sodium hydroxide, potassium or calcium hydroxide, sodium or potassium carbonate, sodium or potassium borate, sodium phosphate, sodium silicate, guanidine hydroxide, or any one of the alkylamines or alkanolamines, for example, ethylamine, triethylamine, tris (hydroxymethyl)methylamine, ethanolamine, diethanolamine, triethanolamine, aminomethylpropanol, aminomethylpropanediol and the like. The preferred alkaline reagents are ammonium hydroxide, sodium carbonate, ethanolamine and aminomethylpropanol. With the reagents listed above, the selected pH will generally be achieved if the composition contains from about 0.1% to 15%, preferably about 0.5% to 5% of an alkaline reagent.

The application of the dyeing components is carried out by methods familiar to those in the art, for example, by mixing the hair dyeing preparation with an oxidant shortly before use, or at the time of applying the mixture onto the hair. On the hair, the compositions form a stable formulation preferably, with enough consistency and body to remain on the hair during the complete coloring period without dripping or running. The primary intermediate and coupler, i.e. the dye precursors, diffuse rapidly into the hair together with the oxidizing agent, or developer. The dyes form within the hair fiber, and since they are large molecules, remain in the hair so that the color change is permanent. The term "permanent" means the dye does not readily wash out of the hair with ordinary shampoos. At the end of coloring application (e.g., approximately 10 to 45 minutes, preferably approximately 30 minutes), the hair is then rinsed then, optionally, shampooed. The application temperature is in the range of about 15° C. to 50° C.

Those in the art will appreciate that the compositions and methods of the present invention are appropriate for the dyeing of keratinous fibers, including the hair fibers of animals and humans, with particular application to the oxidative coloring of human hair.

As mentioned above, the hair dyeing compounds in accordance with the invention produce when coupled a particularly intense color. Dye precursors I and II may be used in conjunction with other primary intermediates and couplers as well as other components, as needed or desired. The colors obtained provide strong fastness to light, shampooing or washing, rubbing or abrasion.

The compositions of this invention may be separately provided in a kit or packaged form ready for mixing by the user, either professional or personal, to initiate the dyeing process. The kit provided in accordance with this invention comprises containers for housing the developer and the dye precursors, such as the primary intermediate(s) and coupler(s). In the most convenient form, there will be two containers, one containing the dye intermediates, e.g., as a lotion; the other containing the oxidizing agent.

The method of the invention comprises applying a mixture of the dye precursors, and other additives if necessary or desired, to the hair to be colored and allowing the resultant composition mixture to remain in contact with the hair until the desired hair color has been attained, after which time the composition is removed from the hair as is conventionally known.

The invention is further described by way of the examples below.

The following comparative compositions A and B were prepared (Table 1)

TABLE 1

Compositions A and B		
	A (%)	B (%)
Water	44.50	44.50
Lactic acid	10.00	10.00
Monoethanolamine	12.00	12.00
Oleic acid	0.50	0.50
Cocamidopropyl betaine	17.00	17.00
Sodium sulfite	0.10	0.10
EDTA	0.10	0.10
Erythorbic acid	0.40	0.40
3-methyl-4-aminophenol	1.00	
4-Aminophenol		0.87
2-Methyl-1-naphthol	1.28	1.28
Water	QS 100	QS 100
Color	Red	Orange-Red

The color uptake (shown in Table 2) was evaluated by the use of the same molar concentration of 4-aminophenol and 2-methyl-1-naphthol. The procedure used is as follows:

100 g of the composition are mixed with 100 g of hydrogen peroxide (20 Volume). The resulting mixture is applied to bleached and gray hair and permitted to remain in contact with the hair for 30 minutes. The thus dyed hair is then shampooed and rinsed with water and dried. Tristimulus values are then determined using a Hunter Tristimulus Colorimeter. L is a measure of lightness and darkness (in other words, the depth of color on the hair tress). The Tristimulus a value is an indicator of the degree of green and red. The Tristimulus b value is an indicator of the degree of yellow and blue.

TABLE 2

	Tristimulus Values of 4-aminophenol derivatives and 2-methyl-1-naphthol					
	gray tress			bleached tress		
	L	a	b	L	a	b
4-Aminophenol	16.74	10.08	4.65	19.47	23.44	8.40
3-methylPAP	16.33	11.42	2.51	15.82	19.08	4.53

#### 1. Wash fastness test

The dyed bleached tresses were immersed in 100 g of 10% Herbal Essences® shampoo from Clairol® and shaken for 3 hours. After rinsing with water, the tress was dried and examined by Hunter Colorimeter. Tristimulus values and overall color changes are reported in Table 3, which follows.

TABLE 3

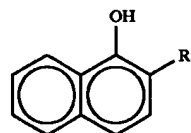
Tristimulus values of 3 hour wash fastness study								
HUNTER VALUES								
Dye	Hair	Before Washing			3 Hour Wash Fastness			ΔE
		L	a	b	L	a	b	
PAP	bleached	19.47	23.44	8.4	32.15	20.86	11.81	13.38
+ 2MN								
3-MePAP	bleached	15.82	19.08	4.53	23.26	21.92	5.74	8.06
+ 2MN								

PAP = 4-aminophenol, 2MN = 2-methyl-1-naphthol  
3-MePAP = 3-methyl-4-aminophenol

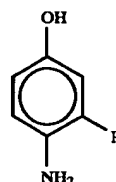
#### We claim:

1. In an oxidative dye composition for dyeing a keratin fiber, the composition containing a primary intermediate, a

coupler, and a cosmetically acceptable vehicle, the primary intermediate and the coupler being present in respective amounts such that in the presence of an oxidizing agent will they react to produce a tinctorially effective amount of an oxidation dye, the improvement comprising the coupler is a 2-substituted-1-naphthol having the formula I



wherein R<sub>1</sub> is C<sub>1</sub>-C<sub>6</sub> alkyl or a monohydroxy C<sub>1</sub>-C<sub>6</sub>-alkyl, and the primary intermediate is a compound of the formula II:



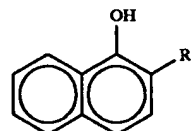
wherein R is a C<sub>1</sub>-C<sub>6</sub> alkyl or a monohydroxy C<sub>1</sub>-C<sub>6</sub>-alkyl.

2. The composition according to claim 1, wherein the compound of formula I is selected from the group consisting of 2-methyl-1-naphthol, 2-ethyl-1-naphthol, 2-propyl-1-naphthol, 2-hydroxymethyl-1-naphthol, 2-(2-hydroxyethyl)-1-naphthol and 2-(3-hydroxypropyl)-1-naphthol.

3. The composition of claim 1, wherein the primary intermediate is 3-methyl-4-aminophenol, 3-ethyl-4-aminophenol, or 3-propyl-4-aminophenol, 3-hydroxymethyl-4-aminophenol, 3-(2-hydroxyethyl)-4-aminophenol or 3-(3-hydroxypropyl)-4-aminophenol.

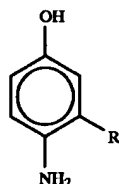
4. The composition according to claim 1, wherein the primary intermediate is 3-methyl-4-aminophenol and the coupler is 2-methyl-1-naphthol.

5. In a method for dyeing hair including the steps of reacting a primary intermediate with a coupler in the presence of an oxidizing agent to produce a tinctorially effective amount of oxidation hair dye and contacting a hair fiber with such dye, the improvement comprising the coupler is a 2-substituted-1-naphthol compound having the formula I:



wherein R<sub>1</sub> is C<sub>1</sub>-C<sub>6</sub> alkyl or a monohydroxy C<sub>1</sub>-C<sub>6</sub>-alkyl, and the primary intermediate is a compound of the formula II:

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wherein R is C<sub>1</sub>-C<sub>6</sub> alkyl or a monohydroxy C<sub>1</sub>-C<sub>6</sub>-alkyl.

6. The method according to claim 5, wherein the compound of formula I is selected from the group consisting of 2-methyl-1-naphthol, 2-ethyl-1-naphthol, 2-propyl-1-naphthol, 2-hydroxymethyl-1-naphthol, 2-(2-hydroxyethyl)-1-naphthol and 2-(3-hydroxypropyl)-1-naphthol.

7. The method according to claim 5, wherein the primary intermediate is 3-methyl-4-aminophenol.

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(II) 8. The method according to claim 5, wherein the primary intermediate is 3-methyl-4-aminophenol and the coupler is 2-methyl-1-naphthol.

5 9. The composition according to claim 1, further comprising at least one material selected from the group consisting of perfumes, antioxidants, sequestering agents, alkalinizing agents, acidifying agents and developers.

10 10. The composition according to claim 1, further containing at least one other primary intermediate or coupler other than I or II.

11. The method according to claim 5, wherein the step of reacting the coupler of formula I with the primary intermediate of formula II is carried out in the presence of at least one other primary intermediate or coupler other than the coupler of formula I or the primary intermediate of formula II.

\* \* \* \* \*